Round-Robin Studies of Two Potential Seebeck Coefficient Standard Reference Materials

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Abstract

The scientific activities of NIST include the development and distribution of standard reference materials (SRM™) for instrument calibration and inter-laboratory data comparison. Full characterization of a thermoelectric material requires measurement of the electrical resistivity, thermal conductivity, and Seebeck coefficient. While standard reference materials exist or have existed for the first two properties, Seebeck coefficient standard reference materials are not available. In an effort to expedite research efforts in this field, we have initiated a project to develop a Seebeck coefficient SRM™ material. Currently, we have completed a round-robin measurement survey of two candidate materials, Bi_2Te_3 and constantan (55% Cu and 45% Ni). In this paper, we summarize our plan and development effort, including the results and the methodology used for the round-robin measurement survey.

Introduction

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. Activities associated with the mission of advancing the standards within the NIST Materials Science and Engineering Laboratory include those which (1) develop, maintain, and retain U.S. primary standards for the structure and properties of materials and provide the means and methods for making measurements consistent with those standards, e.g., develop and distribute reference materials, (2) contribute to the development of technically sound standard test methods by participating in national and international standards developing organizations, and (3) provide critically-evaluated materials data to customers.

Thermoelectric materials are critical for direct energy conversion applications; therefore, the development of standard reference materials for thermoelectric research is essential for U.S. industries. The efficiency of thermoelectric energy conversion or cooling is related to the dimensionless figure of merit (*ZT*) of a thermoelectric (TE) material [1, 2] given by

$$ZT = \frac{\alpha^2 \sigma T}{\kappa}$$

where T is the absolute temperature, α is the Seebeck coefficient or thermoelectric power, σ is the electrical conductivity, and κ is the thermal conductivity. *ZT* is directly related to the coefficient of performance of a thermoelectric material and is the standard criterion by which these materials are judged. Low conversion efficiency has restricted thermoelectric materials to only niche applications. Thermoelectric materials with desirable properties (*ZT* >2, i.e., characterized by high electrical conductivity, high Seebeck coefficient and low thermal conductivity) will have widespread military and industrial applications. In recent years, relatively high *ZT* values have been found in both thin films and bulk materials [3-6]. Continued efforts to identify novel materials and optimize existing materials are crucial for large-scale applications. Most importantly, the accuracy and precision of reported high *ZT* measurements must be confirmed.

Thermoelectric materials characterization is performed through measurements of the electrical resistivity, thermal conductivity, and Seebeck coefficient. Thermal conductivity measurements in particular are often difficult to perform; however, one of the most important initial measurements is that of the Seebeck coefficient. Measurement of only the Seebeck coefficient can filter out those materials that do not have the desired thermoelectric properties (there exists a minimum Seebeck coefficient that must be achieved to give a desired *ZT* [1]). Systems currently being used for measurement of the Seebeck coefficient include both commercial and custom-built systems. While data from different systems is commonly compared, there is no Seebeck coefficient standard reference material for either the low (< 300 K) or high temperature (> 300 K) regime. A Seebeck coefficient SRM would ensure measurement reliability and enable inter-laboratory comparison. Furthermore, a higher level of certainty in the value of the Seebeck coefficient will lead to greater certainty in the value of *ZT*. The low temperature Seebeck material is important for potential

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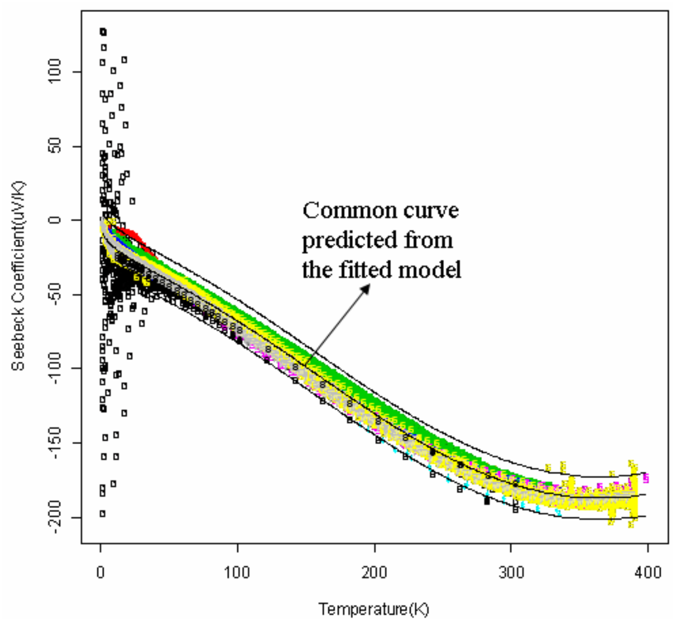

Figure 1: Round robin data sets and the parametric model fitting for Bi_2Te_3 from nine laboratories (excluding three laboratories which provided either less than 5 data points or outlying data). The solid line in the center is the prediction from the fitted model, or the common curve. The two outer lines denote the boundaries defined by the fitted value of $\pm 2\sigma$, where σ is averaged across all temperature values.

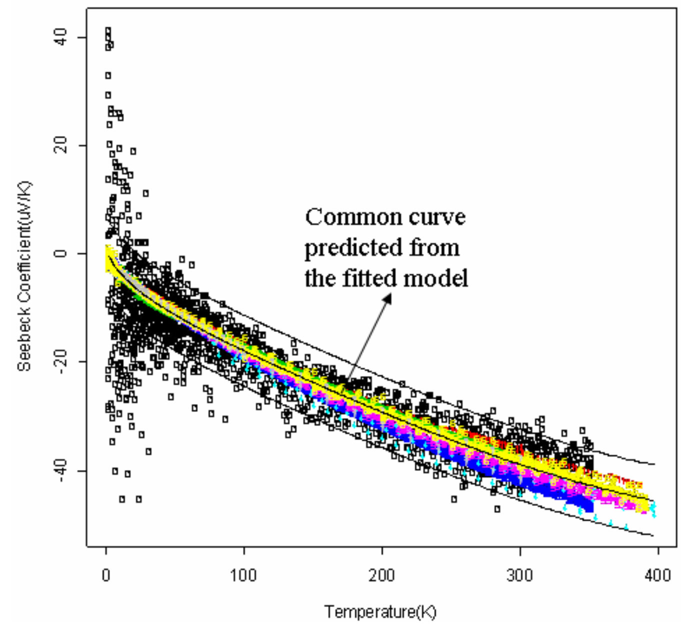

Figure 2: Round robin data sets and the parametric model fitting for constantan from eight laboratories (excluding three laboratories which provided either less than 5 data points or outlying data). The solid line in the center is the prediction from the fitted model, or the common curve. The two outer lines denote the boundaries defined by the fitted value of $\pm 2\sigma$, where σ is averaged across all temperature values.

electronic refrigeration applications, while the high temperature Seebeck material is important for power generation applications. As a first step, we are in the process of developing a Seebeck coefficient standard reference material for the low temperature regime (2-400 K), as well as a procedure for its use. The temperature range covered by this low temperature SRM should provide some crossover with the temperature range of the high temperature equipment as well. Therefore, this low-temperature Seebeck coefficient SRM will provide a full calibration for low-temperature measurement equipment and a partial calibration for high temperature measurement equipment.

Round-Robin Design and Survey

The requirements for a potential Seebeck coefficient SRM include long-term stability, homogeneity, ability to be formed into different geometries, reasonably high Seebeck coefficient values (> 50 μV/K) over a large part of the low temperature regime, and moderate to low thermal conductivity.

Two materials were identified as candidates, undoped Bi_2Te_3 and constantan (55% Cu and 45% Ni alloy). Bi_2Te_3 is a commonly used thermoelectric material with relatively high Seebeck coefficient values (~ 180 μV/K at room temperature), whereas constantan, a common thermocouple material, possesses moderate Seebeck coefficient values (~ 40 μV/K at room temperature).

An international round robin was designed to determine whether Bi_2Te_3 or constantan (or both) should be used as the standard. With this round robin, one can also determine realistic limits on the precision and accuracy of Seebeck coefficient data using various instruments. Cylinders of constantan of 6.47 mm length and 3.45 mm diameter were obtained from Concept Alloys, and rectangular bars of Bi_2Te_3 of 6.08 mm length and 3.04 mm square base were obtained from Marlow Industries. These two potential standards were sent to twelve laboratories that have active thermoelectric research programs (AIST of Japan, Brookhaven National Laboratory, Clemson University, General Motors, Hi-Z Technology, Marlow Industries, Michigan State University, NIST, Quantum Design, Research Triangle Institute, United Technologies, and University of South Florida). The measurement systems used included both custom and commercial apparatus, using a variety of measurement and sample mounting techniques. These will be detailed in a later, more comprehensive report.

The measurement survey consisted of two rounds. Each laboratory was sent a set of samples and asked to perform at least two measurements on each material, using their normal techniques. The samples were then exchanged randomly between the laboratories, and each laboratory measured a second set of samples. This exchange was conducted to provide comparative data between the different measurement techniques as well as check for consistency in the candidate materials. Additional measurements were performed at NIST to provide more comparative data.

Seebeck SRM Round Robin Analysis

Figures 1 and 2 display the Bi_2Te_3 data from nine laboratories and the constantan data from eight laboratories. Data from laboratories which provided less than 5 data points or significantly outlying data was excluded. Since the data will display variability due to different samples and

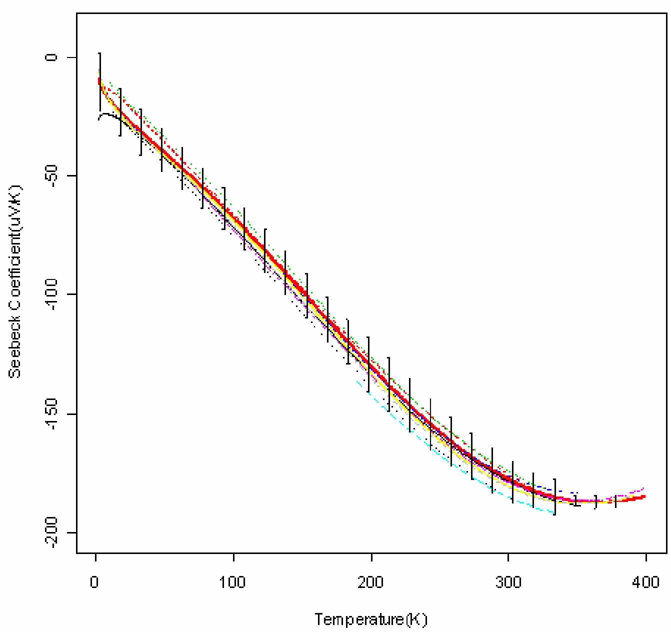

Figure 3: Common fitted curves for individual laboratory data using the parametric model for Bi_2Te_3. The error bars are defined by ± 2σ(T), where σ(T) denotes the variance among the individual laboratory curves at a given temperature T. The common curve (shown in Figure 1) for all laboratory data is also included for comparison.

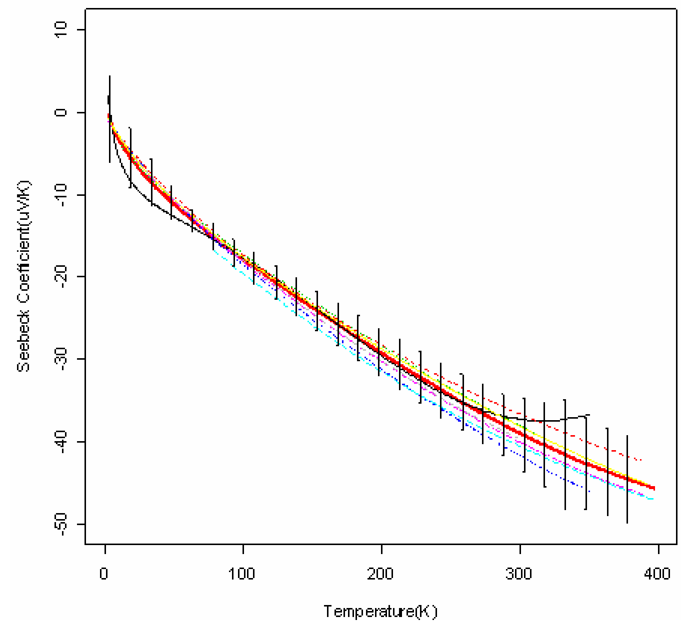

Figure 4: Common fitted curves for individual laboratory data using the parametric model for constantan. The error bars are defined by ± 2σ(T), where σ(T) denotes the variance among the individual laboratory curves at a given temperature T. The common curve (shown in Figure 2) for all laboratory data is also included for comparison.

measurement at different time, temperature, and with different techniques, we need to quantify the variations due to laboratory bias, sample effect, and measurement techniques as a function of temperature. Statistical experimental design will allow us to extract the potential variability [7]. A general model for data fitting from *m* laboratories is as follows:

$$Y_{ij}(t_{ik})=f_0(t_{ik}) + e_{ij}(t_{ik}),\ i=1, \ldots m, j=1,\ldots n_i;\ k=1,\ldots s_i$$

where $Y_{ij}(t_{ik})$ denotes the measurements at temperature points t_{ik} by the ith laboratory on the jth sample, $f_0(t_{ik})$ is the common (true) curve evaluated at t_{ik}, and the measurement errors (including interpolation, laboratory, and sample to sample variability, etc) are summarized by the residual error term $e_{ij}(t_{ik})$, which is assumed to have a normal distribution N(0, $\sigma_i^2(t_{ik})$) for laboratory to laboratory variability, or N(0, $\sigma j^2(t_{ik})$) for sample to sample variability. We use a parametric model for $f_0(t_{ik})$. The purpose of the model is to adequately parameterize the data; there is no physical meaning associated with it. It should be noted that the resulting residual error term $e_{ij}(t_{ik})$ will also contain the lack of fit error due to the use of a parametric model.

The number of datasets included in computing the common fitted curve based on the parametric model is larger than the number of laboratories, as in most cases multiple measurements were performed on each sample. Furthermore, 6 additional samples of Bi_2Te_3 were measured at NIST to provide more sample consistency data. Most Bi_2Te_3 samples included in the measurement survey were also measured at NIST as they were returned. For statistical analysis to obtain the common curve, the Bi_2Te_3 data was taken from 9 laboratories using 34 datasets on 20 different samples; and the constantan data was taken from 8 laboratories using 20 datasets on 12 different samples.

Figures 1 and 2 yield the predicted common curve based on the parametric model as applied to all the data. The solid line in the center is the predicted common curve for all data, and the two outer lines denote the boundaries defined by the fitted value of ± 2σ, where σ is averaged across all temperature values and is thus inflated at higher temperatures but underestimated at lower temperatures. The fit for Bi_2Te_3 is given by

$$f_0 = -57.70 - 2.2 \log(T+1) - 3.2\sqrt{T} - 2.768 \sin(2\pi T/700) + 55.7 \cos(2\pi T/700),\ \sigma=7.2.$$

In this equation, f_0 represents the predicted Seebeck coefficient, and σ is the standard deviation of the residual error $N(0, 7.2^2)$. The R^2 value (ratio of predicted total variance to experimental total variance) is 0.983. The fitted model for constantan, in which the R^2 value is 0.939 (poorer fit), is given as

$$f_0 = -1.076 + 0.5294 \log(T+1) - 2.22\sqrt{T} - 1.160 \sin(2\pi T/700) + 3.248 \cos(2\pi T/700),\ \sigma = 3.3.$$

From these results, it is seen that a σ value of 7.2 μV/K at 300 K corresponds to a coefficient of variation (σ/mean) of ≈4% for Bi_2Te_3 which is smaller than a σ value of 3.3 μV/K (≈ 8%) for constantan at 300K.

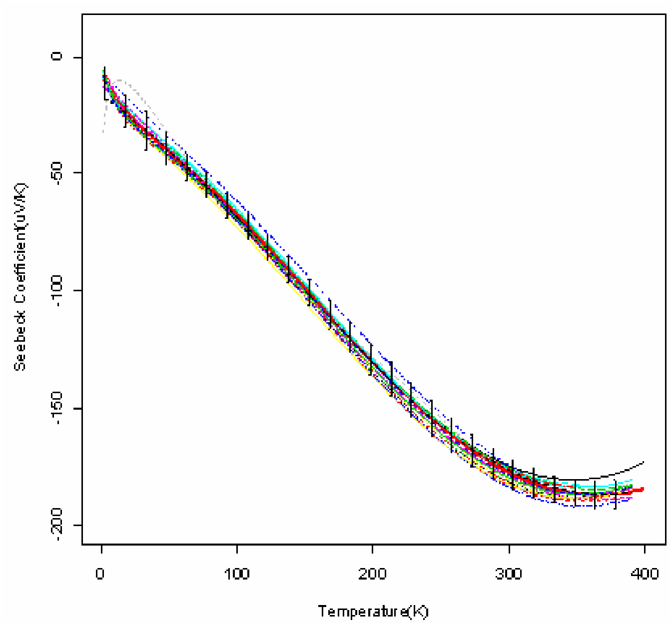

Figure 5: Common fitted curves for individual sample data using the parametric model for Bi_2Te_3. The error bars are defined by ± 2σ(T), where σ(T) denotes the variance among the individual laboratory curves at a given temperature T. The common curve (shown in Figure 1) for all laboratory data is also included for comparison.

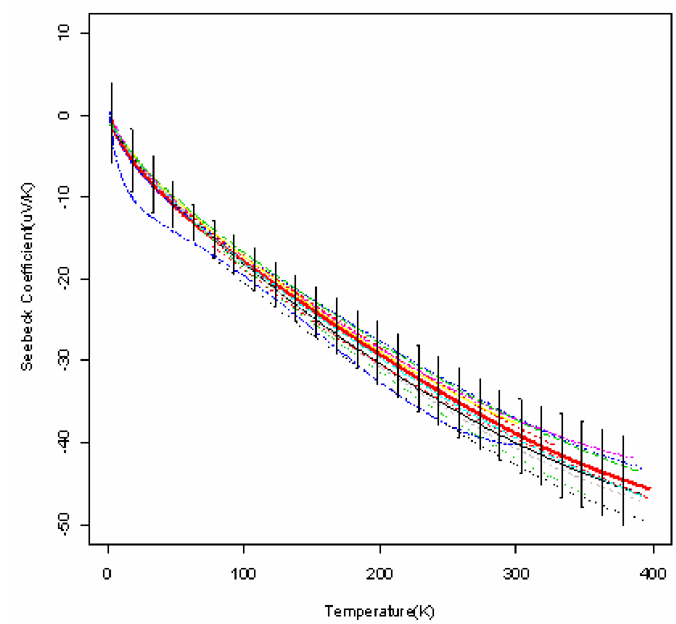

Figure 6: Common fitted curves for individual sample data using the parametric model for constantan. The error bars are defined by ± 2σ(T), where σ(T) denotes the variance among the individual laboratory curves at a given temperature T. The common curve (shown in Figure 2) for all laboratory data is also included for comparison.

We applied a similar parametric model to generate a common fitted curve for each individual laboratory and investigate how these curves compare to the predicted common curve for all data. The common curve for each laboratory is shown as an individual fitted line in Figures 3 and 4 for Bi_2Te_3 and constantan, respectively. The common true curve for all laboratories (same as that shown in Figures 1 and 2) is also shown in these figures for comparison. The error bars are defined by ± 2σ(T), where σ(T) denotes the variance among the individual laboratory curves at a given temperature T. The overall laboratory bias *σ(x)* ranges from 0.77 to 5.09 μV/K for Bi_2Te_3 and from 0.42 to 2.84 μV/K for constantan, as temperature varies. From Figures 3 and 4, we observe that the variance for the Seebeck coefficient remains constant as a function of temperature for Bi_2Te_3 but increases with temperature for constantan. The individual laboratory bias can be estimated by subtracting the common fitted curve from the individual laboratory curves (not shown).

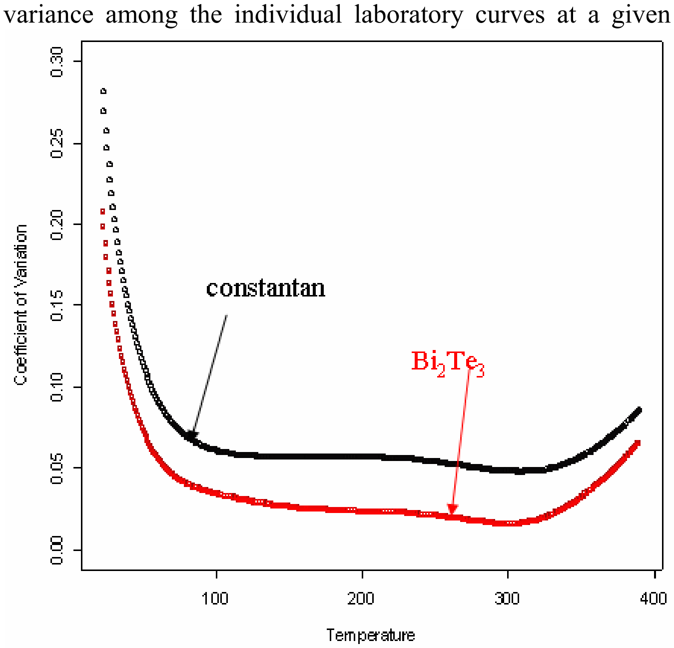

Figure 7: Coefficient of variance (σ(T)/mean) for Bi_2Te_3 and constantan.

By applying similar parametric equations, we also studied the sample effect by obtaining the individual curve fitting for each sample (20 samples for Bi_2Te_3 and 10 samples for constantan). These results are shown in Figures 5 and 6 for Bi_2Te_3 and constantan, respectively. The coefficient of variance for both Bi_2Te_3 and constantan is shown in Figure 7. It is evident from Figure 7 that the coefficient of variance for the Bi_2Te_3 samples is smaller across the entire temperature range as compared to that of the constantan samples.

Based on the above statistical studies and the fact that Bi_2Te_3 yields a much higher Seebeck coefficient, it was the majority decision from the round robin participants that Bi_2Te_3 be the choice for the prototype Seebeck coefficient standard reference material.

Future Certification Plan

A 400 unit batch of Bi_2Te_3 with dimensions 8 x 3.5 x 2.5 mm was recently received from Marlow Industries for certification. These samples are of different size than those used in the round-robin. The modified dimensions will allow more room for the attachment of 4 electrodes, better accommodate resistivity measurements, and reduce measurement errors resulting from the width of the electrodes.

To certify Bi_2Te_3 as the Seebeck SRM, a steady-state DC sweep measurement has been planned. In this technique, the sample is held at a stable temperature; and the temperature gradient across the sample is varied as the voltage difference is measured. This procedure will result in a graph of ΔV vs ΔT, the slope of which will yield the Seebeck coefficient. The data will be reduced, analyzed, and then compared statistically. The statistical model will be designed in collaboration with our NIST statisticians.

Conclusions

We have completed a round-robin measurement survey of 2 candidate Seebeck SRM materials, Bi_2Te_3 and constantan. Based on the results in this study, Bi_2Te_3 was chosen for certification. The Bi_2Te_3 Seebeck SRM should be available to the public in 2008.

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