

# International Round-Robin Study of the Thermoelectric Transport Properties of an *n*-Type Half-Heusler Compound from 300 K to 773 K

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International transport property-measurement round-robins have been conducted by the thermoelectric annex under the International Energy Agency (IEA) Implementing Agreement on Advanced Materials for Transportation (AMT). Two previous round-robins used commercially available bismuth telluride as the test material, with the objectives of understanding measurement issues and developing standard testing procedures. This round-robin extended the measurement temperature range to 773 K. It was designed to meet the increasing demands for reliable transport data for thermoelectric materials used for power-generation applications. Eleven laboratories from six IEA-AMT member countries participated in the study. A half-Heusler (n-type) material prepared by GMZ Energy was selected for the round-robin. The measured transport properties had a narrower distribution of uncertainty than previous round-robin results. The study intentionally included multiple testing methods and instrument types. Over the full temperature range, the measurement discrepancies for the figure of merit, ZT, in this round-robin were  $\pm 11.5$  to  $\pm 16.4\%$  from the averages.

Key words: Thermoelectric, figure of merit, ZT, round-robin

# **INTRODUCTION**

Recent developments in power generation by use of thermoelectric materials have been marked by the transition from laboratory materials research to commercial applications. The most noticeable application is waste heat recovery from automo-

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biles. Only a few candidate materials have been selected, for example skutterudites,<sup>1-6</sup> lead telluride,<sup>7-13</sup> and half-Heusler compounds.<sup>14–26</sup> There also have been efforts to use higher manganese silicide materials (HMS)<sup>27–29</sup> and oxides.<sup>30–36</sup> The maximum values of the figure of merit, *ZT*, of these materials prepared in small batches ranged from 1.0 for half-Heusler compounds<sup>25</sup> to 1.5 for skutterudites<sup>3</sup> and 1.8 for lead telluride.<sup>10,13</sup> For skutterudites, the same materials made in larger (kilogram)

batches for scale-up applications have 10–20% lower  $ZT^{37}$  because of such factors as the purity of the raw materials and processing-related defects. For half-Heusler compounds, materials made in kilogram batches were reported to have the same transport properties as those prepared in small batches.<sup>38</sup> Scaling-up material production while maintaining consistent transport properties is very important for commercialization of thermoelectric power generators. Although pursuing the highest ZT materials is an important aspect of thermoelectricity research, it is also critical to obtain reliable high-temperature transport properties for these materials as input to device and system design. Maximum ZT is not the only factor affecting hightemperature power generation. The ZT over the entire operating temperature range, i.e. average ZTvalues, and the power factor (PF)<sup>38</sup> determine the total power output. Module design requires reliable ZT measurements to determine the optimum power output of each device under a variety of temperature gradients. Thermal resistance between modules and heat exchangers and electrical and thermal losses within the modules reduce the maximum power that can be achieved. Knowing the uncertainties of ZT over the entire temperature range is also important for designing systems with a safe margin and for comparing actual performance with modeled performance.

IEA-AMT round-robins<sup>39,40</sup> performed between 2009 and 2012 were very effective in identifying measurement difficulties and the absence of standardized testing procedures for assessment of thermoelectric properties. After those studies, results from the participating laboratories, especially measurement errors, were analyzed and testing procedures for transport properties measurements were developed. Although the materials tested were commercially available and had very consistent properties, the round-robin showed that measurement errors among the laboratories could be large  $(\pm 15\%$  to  $\pm 21\%$  for ZT). Experimental errors were the largest for thermal conductivity, the error being dominated by specific heat measurement. By development of test procedures substantial improvements were made between the first and second roundrobins. However, the temperature range of the previous round-robins was only from 300 K to 473 K, well below the hot-side temperature for most waste heat recovery applications. To gauge measurement reliability in a higher temperature range, the IEA-AMT thermoelectric annex started the 3rd international round-robin in late 2012. Data collection was completed in June 2014, with results from eleven participating laboratories representing six countries.

## HIGH-TEMPERATURE THERMOELECTRIC MATERIAL SELECTION

Selection of high temperature materials (300-773 K) was conducted before round-robin measurements

began.\* Because no certified reference material (CRM) for thermoelectrics is available in this temperature range, three candidate materials were considered: skutterudites, *n*-type lead telluride, and *n*-type half-Heusler compounds. Skutterudite compounds have been selected by several research groups as candidates for waste heat recovery, and they have high average ZT values and good mechanical properties.<sup>41</sup> However, skutterudites are known to undergo changes as a result of antimony sublimation at high temperatures.<sup>42</sup> Oxidation, especially of p-type materials, can also occur at high temperatures. A round-robin among several laboratories requires samples to be unchanged after each measurement. The potential for sublimation and oxidation of skutterudites, although minimal, was the main reason for not selecting them for this study.

Lead telluride (PbTe) was also considered because it has been used in radioisotope thermoelectric generators (RTG) in National Aeronautics and Space Administration (NASA) space missions.<sup>43,44</sup> *n*-Type lead telluride was evaluated as a round-robin candidate material mainly because of its minimum sublimation and oxidation issues up to 773 K. However, the relatively weak mechanical properties and poor thermal shock resistance made it very difficult to machine and transport to several laboratories. In particular, the very small (4 mm diameter, 1 mm thick) specific heat samples were difficult to prepare, and the samples that did survive the machining process were fragile. It was determined that PbTe was not a suitable material for a thermoelectric round-robin.

The final candidate material was a half-Heusler compound. GMZ Energy developed *n*-type materials by using Ti to partially substitute Hf and reported ZT of approximately 1 at 773 K. The material used in the round-robin had the nominal composition  $Hf_{0.50}Ti_{0.25}Zr_{0.25}NiSn_{0.99}Sb_{0.01}$ . It was prepared by arc melting, ball milling, and hot-press sintering at 1000–1050°C.<sup>25</sup> The half-Heusler material was thermally stable, mechanically strong, and easy to machine. Four sets of materials were prepared. One set was kept at GMZ Energy, and three sets were sent to the Oak Ridge National Laboratory for use in the round-robin study. Of the three sets, one set was circulated among all the laboratories for the roundrobin study and the other two sets were kept as backup samples. Each set contained three specimens for measurement of the transport properties:

- thermal diffusivity: 12.7 mm diameter, 1 mm thick disk;
- specific heat: 4 mm diameter, 1 mm thick disk; and

<sup>\*</sup>Commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the IEA-AMT round-robin participants, nor does it imply that the products identified are necessarily the best available for the purpose.

– Seebeck coefficient and electrical resistivity:  $2 \text{ mm} \times 2 \text{ mm} \times 12 \text{ mm}$  bar.

## MEASUREMENT SYSTEMS AND ROUND-ROBIN

In this round-robin study, 11 laboratories participated over a two-year period. The testing systems used are listed in Table I. For thermal conductivity measurements, eight laboratories used the thermal diffusivity and specific heat methods. There seem to be limited choices of instruments for these two measurements. All the laboratories used testing systems from two commercial suppliers. Thermal conductivity was calculated by use of the equation:

$$k = 100 \alpha D C_{\rm p} \tag{1}$$

in which k is thermal conductivity in W/m K,  $\alpha$  is thermal diffusivity in cm<sup>2</sup>/s, D is density in g/cm<sup>3</sup>, and  $C_p$  is specific heat in J/g K. Two laboratories used direct thermal conductivity measurement methods below 450 K, and one laboratory did not have thermal conductivity testing capability.

All eleven laboratories measured Seebeck coefficient and electrical resistivity; the instruments used are listed in Table I. Five laboratories used the ULVAC ZEM-3 system only, one laboratory used the Linseis system, four laboratories used home-made systems, and one laboratory used both a home-made system and an ULVAC ZEM-3. Unlike the previous round-robins, in which a preponderance of the data were collected by use of ULVAC ZEM systems, in the current round-robin alternative methods were used for more than half of Seebeck coefficient and electrical resistivity measurements. Transport measurement techniques were also divided into twopoint and four-point methods, according to probe arrangement. Several laboratories have both twopoint and four-point options and performed additional testing.

The laboratories in Table I are not identified and the orders of the laboratories in this paper have been re-arranged in each plot. The purpose is not to compare or rank laboratories on testing results, but to focus on data and error analysis. Each laboratory was given instructions to reference the test procedures developed during the past two round-robin studies. Those who performed direct thermal conductivity measurements or used home-made testing systems were asked to use their best practices. Whenever a large discrepancy was observed during data analysis, a laboratory was required to provide system calibration information and reference materials testing data. In this study, all the submitted data from indirect thermal conductivity measurements (obtained by use of Eq. 1) were included in the final calculation of ZT. Direct thermal conductivity measurements were only conducted at temperatures below 450 K, and the results were not used in either for calculation of ZT or for assessment of error propagation.

## **ROUND-ROBIN RESULTS**

## **Electrical Resistivity**

Electrical resistivity of the *n*-type half-Heusler compound was measured by all eleven participating laboratories. The results submitted are shown in Fig. 1a. Nine laboratories used four-point or twopoint measurements for the entire temperature range. The submitted results also included at least three points taken during cooling for those laboratories that measured to 773 K. The cooling data were used to check for possible effects of high-temperature exposure; no changes were observed. Two laboratories used two-point measurements only. The maximum temperature reached was 406 K in one case and 475 K in the other. The processed results are shown in Fig. 1b. Results from nine laboratories were reported at ten designated set points. For measurements results reported away from the set points, linear regression was used to interpolate values from the two nearest points. With nine data points at each set point, no special statistical analvsis was performed other than assuming the results followed a Gaussian distribution. The average

| Laboratory | Thermal diffusivity     | Specific heat    | Seebeck coefficient and resistivity    |  |  |  |
|------------|-------------------------|------------------|--|--|--|--|
| 1          | Netzsch 457             | Netzsch 404      | ULVAC ZEM-3                            |  |  |  |
| 2          | Netzsch 457             | Netzsch 404      | ULVAC ZEM-3                            |  |  |  |
| 3          | Netzsch 457             | Netzsch 404      | Home-made system and ZEM-3             |  |  |  |
| 4          | Netzsch 457             | Netzsch 404      | ULVÁC ZEM-3                            |  |  |  |
| 5          | TA Xplatform            | Netzsch 404      | Linseis LSR3                           |  |  |  |
| 6          | Netzsch 427             | TA Q2000         | Home-made system                       |  |  |  |
| 7          | Anter/TA FL5000         | Netzsch 404      | ULVAC ZEM-3                            |  |  |  |
| 8          | Netzsch 457             | Netzsch 204      | ULVAC ZEM-3                            |  |  |  |
| 9          | Direct thermal conducti | vity measurement | Home-made Harman method                |  |  |  |
| 10         | Direct thermal conducti | vity measurement | Home-made steady-state isotherm method |  |  |  |
| 11         | N/A                     | N/A              | Home-made system                       |  |  |  |

Table I. Testing systems used by participating laboratories



Fig. 1. (a) Electrical resistivity from 11 laboratories for the *n*-type half-Heusler compound. (b) Electrical resistivity from 11 laboratories, showing average values and inter-laboratory uncertainty range ( $\pm 6.5\%$  to  $\pm 7.4\%$ ) for nine laboratories and uncompiled data from two laboratories that used two-point methods.

(arithmetic mean) values were calculated. The standard deviation of the mean  $(\sigma)$  is the result from evaluation of the type  $A^{45}$  uncertainty of the measurement results, which is an indication of consistency between laboratories. We define interlaboratory uncertainty of each measurement at each set point by use of two standard deviations  $(2\sigma, 95\%)$ confidence level), represented by the error bars in Fig. 1b and all other relevant figures. In Fig. 1a and b, the results did not reveal any significant difference between the four-point and two-point methods, which implies that Ohmic contacts are readily formed to the low resistivity, heavily doped half-Heusler material. IEA-AMT procedures<sup>40</sup> require *I–V* measurements to be performed to ensure the establishment of good electrical contact.

The inter-laboratory uncertainties for electrical resistivity were  $\pm 6.5\%$  at 323 K and  $\pm 7.4\%$  at 773 K. The results from two laboratories that used two-point methods at lower temperatures were plotted but not used to calculate the average values and standard deviations. However, both were highly consistent with the average values from the other nine laboratories.

The uncertainty among the laboratories was worse than expected, but not by a large amount. Uncertainties in probe distance measurements or nonuniform current concentration in the sample, depending on the test setups, will affect the results. For example, the voltage probes in all the ZEM systems are the two positive wires of the thermocouple probes. The diameter of the tips of the thermocouples is 0.8 mm. The uncertainty of determining the probe spacing comes from calibration of digital images using a known dimension and manual determination of centers of each probe. We estimate the error could be  $\pm 0.2$  mm. With typical spacing of 5.0 mm, the error from measurement of probe spacing can be  $\pm 4\%$ . The variations in electrical resistivity measurements indicate the need for further development of standard reference materials, standardization of test procedures, and improvement of commercial testing systems.

#### **Seebeck Coefficient**

Seebeck coefficient also was measured by all participating laboratories. All the results submitted are shown in Fig. 2a, including two two-point measurements up to 773 K and two lower-temperature two-point measurements up to 406 K and 475 K. Although data scatter was substantial, the results from the two-point measurements were clearly lower than those from the four-point measurements. Figure 2b shows the processed results from four-point measurements by nine laboratories. Similar to resistivity, the average values and standard deviations were calculated at ten designated points. The plotted measurement error bars represent  $\pm 2\sigma$  inter-laboratory uncertainty ranging from  $\pm 5.7\%$  to  $\pm 7.9\%$ .

The results from the two-point measurements are shown in Fig. 2c. The four points at lower temperatures were calculated by using data from four laboratories; the higher-temperature results were averages from two laboratories only. To reveal differences between the four-point and two-point measurements, the average values obtained from the two methods are plotted at the same ten points in Fig. 2d. The differences between the two methods ranged from 11.3% to 13.6%, with results from the two-point method consistently lower than those from the four-point method. This particular topic, i.e. the bias between four-point and two-point methods, has been discussed by Martin et al.<sup>46</sup> They attributed the differences mainly to leakage of heat through the contact probes, which causes underestimation of  $\Delta T$  for the four-point method, resulting in higher Seebeck values. The two-point method gives lower Seebeck values because of overestimation of  $\Delta T$ , but this effect can be minimized by use of good contacts. On the basis of this analysis,<sup>46</sup> although the true value is likely to be between those obtained by use of these two methods, it is also likely to be much closer to that obtained by use of



Fig. 2. (a) Seebeck coefficient from 11 laboratories for the *n*-type half-Heusler material. (b) Seebeck coefficient from nine laboratories using a four-point method, showing average values and inter-laboratory uncertainty range (+5.7% to +7.9%). (c) Seebeck coefficient from four laboratories using two-point methods, showing average values and inter-laboratory uncertainty range (+0.6% to +7.6%). (d) Seebeck coefficients from nine laboratories using four-point methods versus four laboratories using two-point methods (two laboratories used both a four-point method at two-point method).

two-point arrangement. Although modification and calibration can be used to furnish more accurate Seebeck values, that was not the purpose of this study. Another source of uncertainty for the Seebeck coefficient could be the Seebeck value of the thermocouple wire. After high-temperature measurements, diffusion could occur between the sample and the probes, making the original calibration values for wire Seebeck coefficient incorrect. This drift could vary from laboratory to laboratory depending on the materials tested. If the original wire Seebeck values were applied, the final Seebeck results could include these errors. These large variations in Seebeck coefficient measurements must be addressed by further development of standard reference materials, standardization of test procedures, and improvement of commercial testing systems.

## **Thermal Diffusivity**

Thermal diffusivity of the GMZ material was measured by eight laboratories, by use of the laser flash diffusivity method. All the laboratories used either the Netzsch or the TA Instrument laser flash systems. These commercial systems are designed for use in accordance with the method described in ASTM 1461.47 The results are shown in Fig. 3a, including data points taken during cooling to ensure the sample was not changed by exposure to high temperatures. The results were very consistent among all the laboratories. Data processing was performed for ten designated points by using the heating data only. A few laboratories reported raw data offset from the ten designated points because of the temperature difference between the instrument set point and the actual testing temperature. Linear curve fitting and interpolation were used to calculate the values at the set points. The results are shown in Fig. 3b. The error bars are  $\pm 2\sigma$  standard deviations from the average values. The inter-laboratory uncertainty among the eight laboratories was  $\pm 1.9\%$  at 323 K and  $\pm 3.7\%$  at 773 K. This was a substantial improvement on previous round-robin results, for which scatter among the laboratories was nearly  $\pm 10\%$ . By keeping the flash energy at low to moderate levels, the measured values had less distortion in the temperature-to-voltage conversion of the infrared detector signals, thus making measurements of the half-rise time more accurate. The sample was carefully machined to have parallel faces, thus minimizing the measurement error in sample thickness. Because sample



Fig. 3. (a) Thermal diffusivity results from eight laboratories for the *n*-type half-Heusler material. (b) Thermal diffusivity from eight laboratories, showing average values and inter-laboratory uncertainty range (+1.9% to +3.7%).

thickness was carefully chosen for the round-robin, the decrease in measurement errors were mainly because of the use of lower laser energy.

## **Specific Heat Capacity**

Specific heat was measured by use of differential scanning calorimeters (DSC) to enable calculation of thermal conductivity by use of Eq. 1. In the previous round-robin studies,  $C_{\rm p}$  was identified as the property most difficult to measure with good reproducibility. The test procedures developed by the IEA group at the conclusion of the first round-robin were used as guidance. The results submitted by eight laboratories are shown in Fig. 4a. Significant scatter still exists among the results. The most obvious difference is the general slope of the plot of  $C_{\rm p}$  as a function of T. This scatter is an indication that instrument baselines were not stable. This is more of an instrument-operation variable, because it is difficult to determine when a specific instrument is sufficiently stable to conduct measurements. The raw data were processed to calculate average values at ten designated points, as shown in Fig. 4b. The error bars represent  $2\sigma$  standard deviation. The



Fig. 4. (a) Specific heat from eight laboratories for the *n*-type half-Heusler compound. (b) Specific heat from eight laboratories, showing average values and reproducibility range (+5.6% to +10.0%), and the Dulong–Petit limit of  $C_{v}$ .

inter-laboratory uncertainty for  $C_{\rm p}$  was  $\pm 5.6\%$  at 323 K and  $\pm 10.0\%$  at 773 K. On the basis of crystal structure and composition, the Dulong–Petit limit (3NR, where N is the number of moles and R is the universal gas constant) of  $C_{\rm v}$  for the *n*-type half-Heusler compound was calculated to be 0.248 J/g-K. It is a constant value and is plotted at each point in Fig. 4b. It is interesting to see the 3NR values are much closer to the eight-laboratory average than the experimental scatter. This suggests that, for the *n*-type half-Heusler compound, which has a low Debye temperature, it may be reasonable to calculate thermal conductivity by using the Dulong–Petit limit when DSC measurement of  $C_{\rm p}$  is not available. At least, the 3NR value should be calculated as a validation check of measured  $C_{\rm p}$  values.

#### FIGURE OF MERIT AND UNCERTAINTY ANALYSIS

The *n*-type half-Heusler material was the best thermoelectric candidate for a round-robin study in the temperature range 300-773 K. An ideal round-robin study would have followed guidelines of the International Organization for Standardization (ISO).<sup>48</sup> However, the lack of CRM for thermoelectrics and proper CRM (similar reference values in the temperature range of interest) for the individual test method made complete uncertainty analysis difficult. For example, the repeatability, reproducibility, and trueness of most instruments for thermoelectrics are unknown. Some laboratories provided measurement uncertainties in the report, some quoted uncertainties for the instruments provided by the vendor. The information and reporting are not standardized. It is the intention of the IEA-AMT group to make these measurements and procedures standardized. The lack of CRM and test standards is reflected in the difficulty of analyzing the round-robin results. Given the experimental results from each laboratory, the initial analysis focused on inter-laboratory uncertainty.

The figure of merit was calculated by using the equation for  $ZT = S^2 T/\rho k$  in which S is the Seebeck coefficient,  $\rho$  is the electrical resistivity, T is temperature in Kelvin, and k is thermal conductivity.  $S^2/\rho$  is also known as the PF. The values were calculated by using Seebeck coefficient and electrical resistivity data from the nine laboratories that completed testing in the entire temperature range. As shown in Fig. 5a, the  $2\sigma$  error bars (inter-laboratory uncertainty) for the PF ranged from  $\pm 13.4\%$  to  $\pm 17.5\%$ .

Error propagation for the PF, was calculated by use of the equation:

$$2\sigma_{\rm PF} = \sqrt{4(2\sigma_s)^2 + (2\sigma_\rho)^2} \tag{2}$$

The values for each temperature are shown in Table II. In Eq. 2, we ignored a negative correlation error term for  $S^2/\rho$ , i.e.  $-2\sigma_{s\rho}/s\rho = 0$ . Although it is safe to assume this term to be zero for independent properties, it is not correct when measurements of S and  $\rho$  share the same probes on the same specimen. Because all the laboratories measured these two properties at the same temperature and reported a calculated PF, the correlation term is embedded in the data. In Fig. 5a, the PF of the nine laboratories were calculated first and then plotted at the ten set points. The  $2\sigma$  error bars for the direct PF ranged from  $\pm 9.1\%$  to  $\pm 14.0\%$ . An average decrease of 3.1% in the error bars indicated a strong correlation between Seebeck coefficient and electrical resistivity measurement errors.

Thermal conductivity, k, is calculated (via Eq. 1) by using the corresponding  $2\sigma$  error propagation:

$$2\sigma_{k} = \sqrt{(2\sigma_{\alpha})^{2} + (2\sigma_{Cp})^{2} + (2\sigma_{D})^{2}}$$
(3)

On the basis of the geometry of the bar specimen  $(2.540 \text{ mm} \times 2.568 \text{ mm} \times 12.287 \text{ mm})$  and its weight (0.711 g), the uncertainty of the micrometer (0.005 mm) and balance (0.0005 g), and machining tolerance, the density measurement had an uncertainty of  $\pm 0.4\%$ . This was not an inter-laboratory uncertainty. Because the value is very small compared with thermal diffusivity and specific heat, it



Fig. 5. (a) Power factor from nine laboratories using the four-point method, showing average values and inter-laboratory uncertainty range (+13.4% to +16.4%), calculated both directly and via error propagation of the Seebeck coefficient and electrical resistivity uncertainties. (b) Thermal conductivity from eight laboratories using flash diffusivity and the DSC method, showing average values and inter-laboratory uncertainty range (+6.4% to +10.4%). (c) Figure of merit from nine laboratories using the four-point method, showing average values and inter-laboratory uncertainty range (+11.6% to +10.4%).

does not affect the round-robin conclusions. Equation 3 gives  $2\sigma$  error values for thermal conductivity ranging from  $\pm 6.3\%$  to  $\pm 10.4\%$ , as shown in Fig. 5b. The values for all the designated temperatures are listed in Table II. It should be noted that two

Table II. Round-robin uncertainties based on data scatter (maximum scatter from the mean value divided by the mean value). The uncertainties for density and temperature are assumed to be constant over the temperature range

| Temp (K) | α (%) | C <sub>p</sub> (%) | <b>D</b> (%) | к (%) | ρ (%) | <b>S</b> (%) | <b>PF</b> (%) | Direct PF (%) | T (%) | ZT (%) |
|----------|-------|--------------------|--------------|-------|-------|--------------|---------------|---------------|-------|--------|
| 323.0    | 3.7   | 5.6                | 0.4          | 6.8   | 6.5   | 5.9          | 13.4          | 13.6          | 1.0   | 15.3   |
| 373.0    | 2.6   | 5.8                | 0.4          | 6.3   | 7.5   | 7.9          | 17.5          | 14.0          | 1.0   | 15.4   |
| 423.0    | 2.4   | 6.7                | 0.4          | 7.1   | 8.0   | 7.1          | 16.4          | 12.2          | 1.0   | 14.2   |
| 473.0    | 2.3   | 7.4                | 0.4          | 7.8   | 9.1   | 6.0          | 15.0          | 12.5          | 1.0   | 14.8   |
| 523.0    | 2.2   | 7.5                | 0.4          | 7.8   | 9.0   | 6.8          | 16.4          | 13.0          | 1.0   | 15.2   |
| 573.0    | 1.9   | 6.8                | 0.4          | 7.1   | 8.3   | 5.7          | 14.1          | 9.1           | 1.0   | 11.5   |
| 623.0    | 2.0   | 7.3                | 0.4          | 7.6   | 7.8   | 6.2          | 14.7          | 9.7           | 1.0   | 12.3   |
| 673.0    | 2.5   | 8.5                | 0.4          | 8.8   | 8.0   | 5.7          | 13.8          | 10.4          | 1.0   | 13.7   |
| 723.0    | 3.1   | 9.3                | 0.4          | 9.8   | 7.6   | 6.2          | 14.6          | 11.2          | 1.0   | 14.9   |
| 773.0    | 3.1   | 10.0               | 0.4          | 10.4  | 7.4   | 5.7          | 13.5          | 12.6          | 1.0   | 16.4   |

laboratories made direct measurements of thermal conductivity. One laboratory measured to 405 K and the results matched the first three data points in Fig. 5b very well. The other laboratory measured up to 500 K and the results were consistently more that 30% higher than the round-robin averages. Because of the lack of system calibration and further validation with reference materials the results were not included. With one set of valid data left, the direct thermal conductivity results were not used in the final statistical analysis and *ZT* calculations.

Finally, inter-laboratory uncertainty of ZT was calculated by use of the error propagation (Eq. 4):

$$2\sigma_{ZT} = \sqrt{(2\sigma_{\rm PF})^2 + (2\sigma_k)^2 + (2\sigma_T)^2}$$
 (4)

Similar to density measurement uncertainty, the estimated uncertainty for temperature measurement is  $\pm 1\%$  which is typical for thermocouples. We used the direct PF errors in Eq. 4. The results are shown in Fig. 5c, with the  $2\sigma$  error bars for interlaboratory uncertainty of *ZT* ranging from  $\pm 11.5\%$  to  $\pm 16.4\%$ . Although error analysis was not performed, because of the small data sets available, it should be noted that the Seebeck coefficient was 11.3-13.6% lower for the two-point method, the final average *ZT* could be 19.2–22.4\% lower.

The values are listed in Table II. Compared with the  $\pm 21\%$  experimental scatter found in the earlier round-robin,<sup>40</sup> the improvement was substantial. The temperature range is more than doubled for the half-Heusler material compared with that for the bismuth telluride. Although this inter-laboratory uncertainty may seem large, it is in fact quite remarkably low considering that the figure of merit, ZT, is calculated from four properties—three directly measured quantities  $(S, \rho, \text{ and } T)$ , and one other property, thermal conductivity, that is calculated from three other measured values  $(\alpha, C_p, \text{ and } D)$ . Each measurement includes experimental uncertainty, and therefore ZT includes uncertainties of temperature and six measured properties. The potential for large uncertainties in ZT is because of the difficulty of measurement of transport properties and error-propagation rules. To reduce the uncertainty in ZT, several property measurements must be improved. The final error bar for ZT cannot be smaller than the largest individual error bar. For ZT calculation, three properties (electrical resistivity, Seebeck coefficient, and specific heat) each included 9-10% individual uncertainties, leading to large error bars for the final values. It was observed by error analysis that the directly calculated PF error bars are smaller than those predicted by treating Seebeck coefficient and electrical resistivity measurements as uncorrelated. The reduced uncertainty when several measurements are performed on a single specimen suggests the correlation factor in the error propagation is important. Similar to the negative correlation term for the PF, thermal conductivity is also in the denominator of the ZT calculation. If thermal conductivity can be obtained from the same specimen as the Seebeck coefficient and electrical resistivity, the uncertainty for ZT could be reduced. For a single-specimen set up, the geometry factors used to calculate resistivity and thermal conductivity will cancel out, further reducing the uncertainty of ZT.

To estimate the uncertainties, each laboratory has a variety of internal reference materials (stable over the long term) or reference materials (RM) supplied by the instrument vendors. These RM are necessary to maintain the measurement repeatability of each laboratory. In some cases, certified reference materials (CRM) are available for some properties. For example, a thermal diffusivity and thermal conductivity CRM, BCR-724 glass-ceramic (Pyroceram 9606) was certified by the European Commission.49 The uncertainty (expanded uncertainty, coverage factor k = 2, confidence level 95%) was  $\pm 6.1\%$  for thermal diffusivity,  $\pm 7\%$  for specific heat, and  $\pm 6.5\%$  for thermal conductivity (direct thermal conductivity measurements). For Seebeck materials, a traceable material, CuNi<sub>44</sub> Mn<sub>2</sub>-alloy Isostan, was certified with uncertainty of  $\pm 5\%$ .<sup>50</sup> However, no CRM is available for electrical

resistivity. A recent analysis by Mackey<sup>51</sup> on electrical resistivity and Seebeck coefficient put the uncertainties at  $\pm 7\%$  for electrical resistivity,  $\pm 1.0\%$  to  $\pm 13\%$  for Seebeck coefficient, and  $\pm 7.3\%$  to  $\pm 27.0\%$  for the PF.

These uncertainties  $(\pm 5\% \text{ to } \pm 7\%)$  for available CRM are generally acceptable for individual laboratory studies, and are often used by commercial instrument suppliers. Lack of a CRM for electrical resistivity or a single CRM for thermoelectrics makes the combined uncertainty of ZT difficult to estimate. Analysis and modeling for  $PF^{51}$  and previously identified operator-dependency for specific heat<sup>40</sup> estimate the uncertainty in ZT as larger than  $\pm 20\%$ . This is precisely the reason for conducting this international round-robin. The current IEA-AMT round-robin has shown that inter-laboratoryuncertainty for ZT is, on average,  $\pm 14\%$  ( $\pm 11.5\%$  to  $\pm 16.4\%$  in the 300–773 K range). It is important for the thermoelectric community to recognize the current measurement limitations and uncertainties. Improvements in measurement techniques, and test procedures are necessary for more reliable evaluation of material performance. Future round-robin efforts should include materials and measurement to at least 1000 K to cover a higher temperature range.

#### CONCLUSIONS

This international round-robin study by IEA-AMT on an *n*-type half-Heusler material covered the temperature range 300-773 K, as relevant to automotive waste heat recovery. It revealed critical measurement reproducibility for the figure of merit, ZT, a property essential for the design of thermoelectric modules and thermoelectric generators. The round-robin also showed that comparable uncertainties in results for several properties make the errors in ZT substantially larger than for any single property. Compared with an earlier round-robin, thermal diffusivity measurement uncertainty dropped from  $\pm 8-10\%$  to  $\pm 3-4\%$ , indicating it is possible to improve measurement reproducibility. Modest improvement was observed for specific heat measurement, but the system baseline stability error and other operator-related errors should be reduced. Electrical resistivity and Seebeck coefficient need further improvement in measurement techniques and system calibration with standards. It is therefore expected that reproducibility standard deviation may be at least 20% for most materials reported. This is important for inter-laboratory comparison, but development of new materials in each individual laboratory is still possible because the repeatability standard deviation for ZT is likely to be below ten percent.

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