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Reduction of Specimen Size for the Full Simultaneous Characterization of Thermoelectric Performance

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The successful implementation of thermoelectric (TE) materials for waste heat recovery depends strongly on our ability to increase their performance. This challenge continues to generate a renewed interest in novel high TE performance compounds. The technological difficulties in producing homogeneous ingots of new compounds or alloys with regular shape and a size sufficiently large to prepare several samples that are usually needed for a separate measurement of all TE parameters are well known. It creates a situation whereby material performance could be critically over- or under-evaluated at the first stages of the research process of a new material. Both cases would equally lead to negative consequences. Thus, minimizing the specimen size yet keeping it adequate for accurate material characterization becomes extremely important. In this work we report the experimental validation of reliable simultaneous measurements of the four most relevant TE parameters on a single bismuth telluride alloy based specimen of 4 mm × 4 mm × 1.4 mm in size. This translates in roughly 140 mg in weight for one of the heaviest TE materials, as was used in this study, and <100 mg for most others. Our validation is based on comparative measurements performed by a Harman apparatus (ZT-Scanner) on a series of differently sized specimens of hot extruded bismuth telluride based alloys. The Seebeck coefficient, electrical resistivity, thermal conductivity and the figure of merit were simultaneously assessed from 300 K to 440 K with increments of 20 K, 15 K, 10 K, 5 K, and 1 K. Our choice of a well-known homogeneous material has been made to increase measurement reliability and accuracy, but the results are expected to be valid for the full TE characterization of any unknown material. These results show a way to significantly decrease specimen sizes which has the potential to accelerate investigation of novel TE materials for large scale waste heat recovery.

Key words: Figure of merit, thermoelectric measurements, ZT-Scanner, Harman method

INTRODUCTION

Thermoelectric (TE) generators can be used in large scale applications to convert waste heat into electricity, thus generating electrical power. Several classes of thermoelectric materials such as tellurides,[1,2] half-Heuslers,[3,4] silicides,[5,6] and tetrahedrite[7] alloys were investigated for this purpose. Frequently, however, accurate and rapid evaluation of their performance remains challenging. This may slow down decision processes when comparing advantages and drawbacks of specific TE materials.

It is a commonly accepted practical rule that to increase the repeatability of the result of any measurement it is convenient to prepare samples with the same shape and similar size. This statement is

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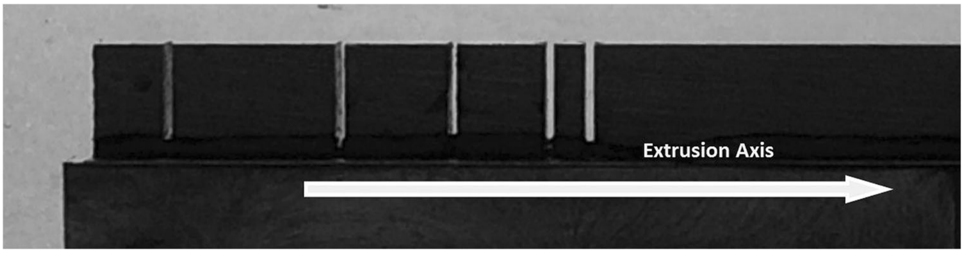

Fig. 1. Four samples cut for this study from a long $(Bi_{0.95}Sb_{0.05})_2$ $(Te_{0.95}Se_{0.05})_3$ bar of hot extruded material. Their lengths are 7.15 mm, 4.4 mm, 3.38 mm, and 1.41 mm. Both end pieces are excluded.

specifically important for the characterization of thermoelectric materials when thermal exchange between the sample and its environment will influence the results. Several round-robin tests have been performed in the past[8–10] aiming to evaluate accuracy and reproducibility of TE measurements and to elaborate a standard measurement procedure. All these studies were concentrated on separate measurements of electrical resistivity (ρ), Seebeck coefficient (α), thermal diffusivity, and specific heat (C_p). The sample configurations used for round-robin tests were as follow: bars 2 mm × 2 mm × 12–15 mm for ρ and α measurements, discs 1 mm thick and 12.7 mm-diameter for thermal diffusivity and 1 mm-thick × 4 mm-diameter for C_p. However, those configurations only fit well-established material manufacturing technologies able to produce a relatively large volume of homogeneous material from which it is possible to cut the above three differently shaped samples respecting the same direction of measurements for all parameters (minimum 13 × 13 × 16 mm^3 to produce the full set of samples corresponding to.[8–11] This is far from the most common research practice where small sized samples are usually available with only one specific shape (often irregular). They could be disc shaped specimens produced by spark plasma sintering (SPS) technology and hot pressing or arbitrarily shaped fragments of grown ingots. It is always extremely challenging to produce homogeneous bulk material at the early stages of exploration of new compounds. Therefore finding an accurate evaluation of the dimensionless figure of merit (ZT), electrical resistivity, Seebeck coefficient, and thermal conductivity on one small sample and in the same direction (in case of anisotropy) becomes a key factor accelerating the research process in thermoelectricity. We demonstrate in this study the ability of the ZT-Scanner,[12,13] a setup that is based on the Harman method,[14] to deliver reliable data from 300 K to 440 K on a single specimen as small as 4 mm × 4 mm × 1.4 mm in volume, or about 140 mg in weight in a case of bismuth telluride based alloy.

EXPERIMENTAL

All measurements in this study were performed on the ZT-Scanner (TEMTE Inc.), which was described in details in our earlier publications.[12,13] This fully automated system allows the simultaneous measurement of ZT, α, ρ, and the thermal conductivity λ from 300 K to 720 K on the same sample. A highly homogeneous hot extruded $(Bi_{0.95}Sb_{0.05})_2$ $(Te_{0.95}Se_{0.05})_3$ material[15,16] was used for sample preparation to ensure similarity of their properties. A long bar with a square section of 5 mm × 5 mm was cut in the direction of the extrusion axis from the central section of a rod 25 mm in diameter. Four samples with the lengths of 7.15 mm, 4.4 mm, 3.38 mm, and 1.41 mm were then cut from this bar with a low speed diamond blade as it is shown in the image of Fig. 1. The surfaces designated for contact plating were electropolished in solution of 56 g sodium hydroxide + 48 g tartaric acid + 570 ml distilled water with a direct current (DC) current density of about 500 mA/cm. A nickel layer 5 μm-thick was brazed at 300°C with a 10–15 μm thick $Pb_{0.60}Sn_{0.40}$ alloy, immediately after electroplating, to facilitate sample mounting.

The thermoelectric measurements were carried out under a vacuum of 0.2–0.5 kPa with a DC current of 100 mA.[12,13] The temperature scan was limited to the 300–440 K range because of the low melting point of PbSn soldering alloy. Temperature increments of 1 K, 2 K, 5 K, 10 K, 15 K, and 20 K were used to verify reproducibility of the measurements. A 40 min interval allows for temperature stabilization on each step in all cases. Temperature runs on each sample were made in one sequence without opening the vacuum chamber and avoiding sample reinstallation to reduce possible influence of operator manipulations.

RESULTS AND DISCUSSION

The reproducibility of the measurements taken with a ZT-Scanner was already demonstrated in previous work;[12,13] however, we have performed additional tests to validate the present study. One of the samples with a length of 7.15 mm after routine scan with steps of 15 K was subjected to four consecutive temperature scans from 300 K to 440 K with temperature increments of 1 K, 5 K, 10 K, and 20 K, respectively. We have reduced the maximum temperature from 450 K, used in Ref. 13 to avoid the observed negative influence of diffusion of PbSb soldering alloy through the Ni layer, which has an impact on the electrical resistivity and the ZT value. Because we are now preventing contact degradation at high temperatures the results for different temperature runs in the present study are getting so close that for the purpose of better visibility Fig. 2 shows the temperature variations of the main thermoelectric parameters only for the two most different increment steps: of 1 K and 20 K. Please notice the ability of this instrument to provide sample characterization with a resolution of 1 K. Table I shows another example of reproducibility of measurements. The relative standard deviations of the experimental points from the third order polynomial tendency curves for α, ρ, λ, and ZT values, assessed with increments of 15 K and 2 K, were calculated for the sample 4.4 mm in length, and presented in Table I. The bottom row of the table shows the relative standard deviations of the measured TE parameters evaluated by comparison of two tendency curves corresponding to the measurements with increment steps of 15 K and of 2 K.

Clearly, the reproducibility of the tests for the four TE parameters is better than 1% as it can be seen from Table I, which is necessary for a comparative analysis on different samples. Taking into account that the tendency curves are always within

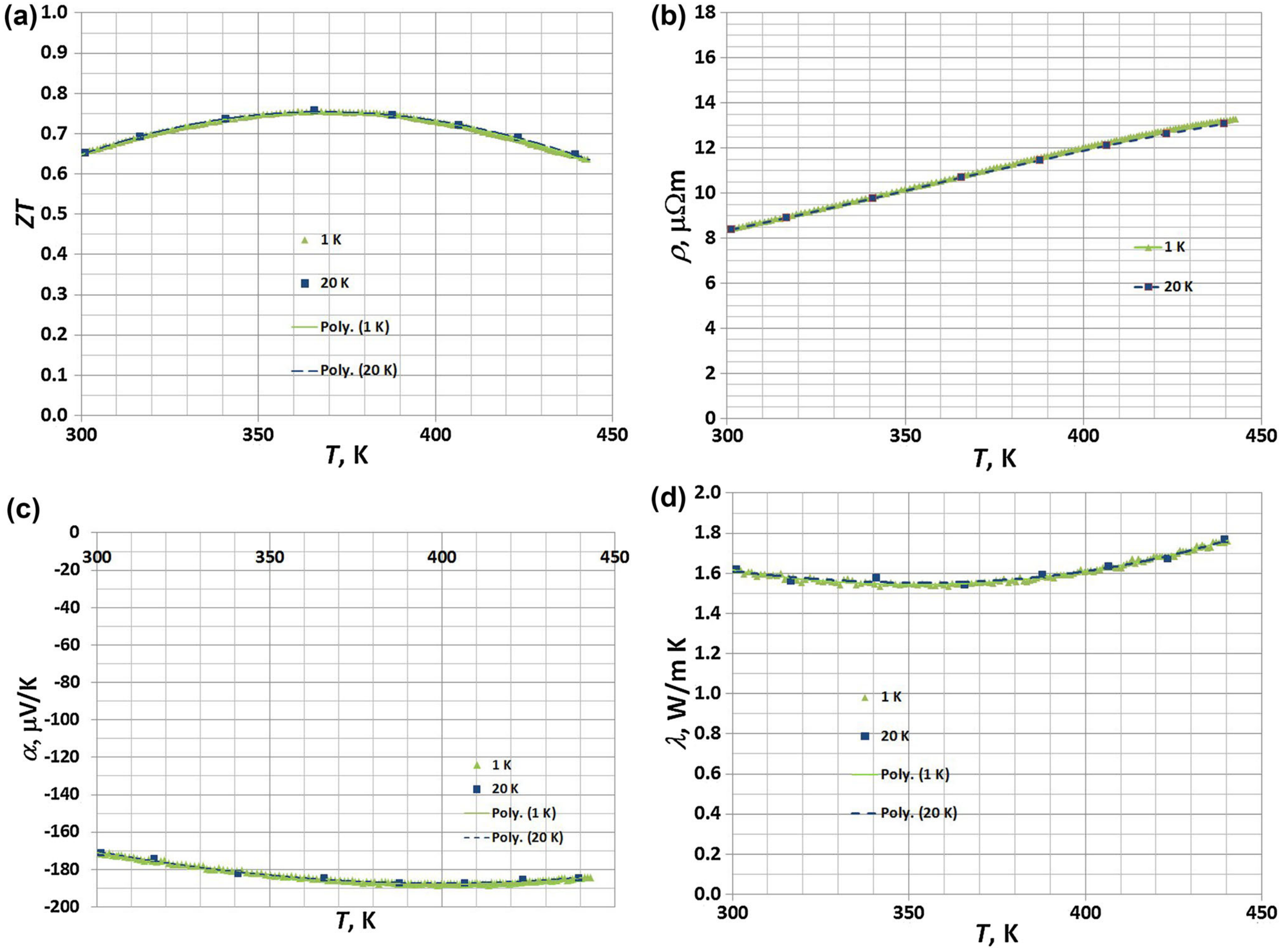

Fig. 2. Temperature variations of ZT (a), ρ (b), α (c), and λ (d) of the $(Bi_{0.95}Sb_{0.05})_2$ $(Te_{0.95}Se_{0.05})_3$ sample with the length of 7.15 mm. For clarity only the measurements with increment steps of 1 K and 20 K are shown. Continuous lines labeled Poly (...) represent 3rd order polynomial tendency curves determined from these measurements.

Table I. Statistical analysis of two consecutive measurements of the $(Bi_{0.95}Sb_{0.05})_2$ $(Te_{0.95}Se_{0.05})_3$ sample 4.4 mm in length from 300 K to 440 K with the increment steps of 15 K and 2 K

Value	α, μV/K (%)	ρ, μΩm (%)	λ, W/(m K) (%)	ZT (%)
Rel. SD 15 K	0.18	0.05	0.43	0.22
Rel. SD 2 K	0.21	0.047	0.51	0.18
Rel. SD 15 K versus 2 K	0.29	0.64	0.76	0.24

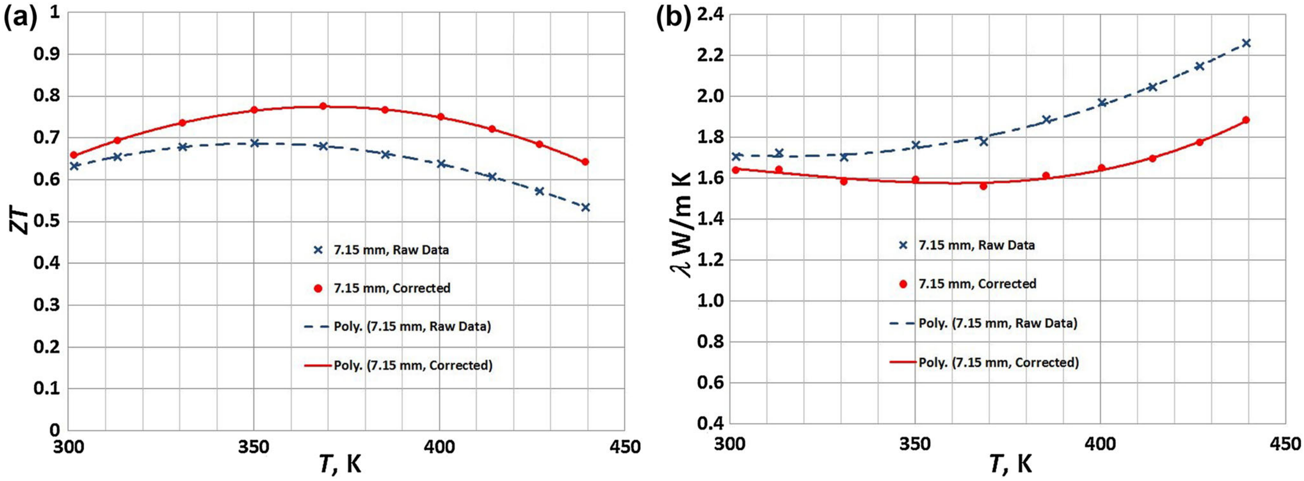

Fig. 3. Variation with temperature of raw (crosses and dashed tendency curve) and corrected (solid circles and continuous line) values of ZT (a) and λ (b) measured now with the increment steps of 15 K on the same sample as for Fig. 2 with the length of 7.15 mm.

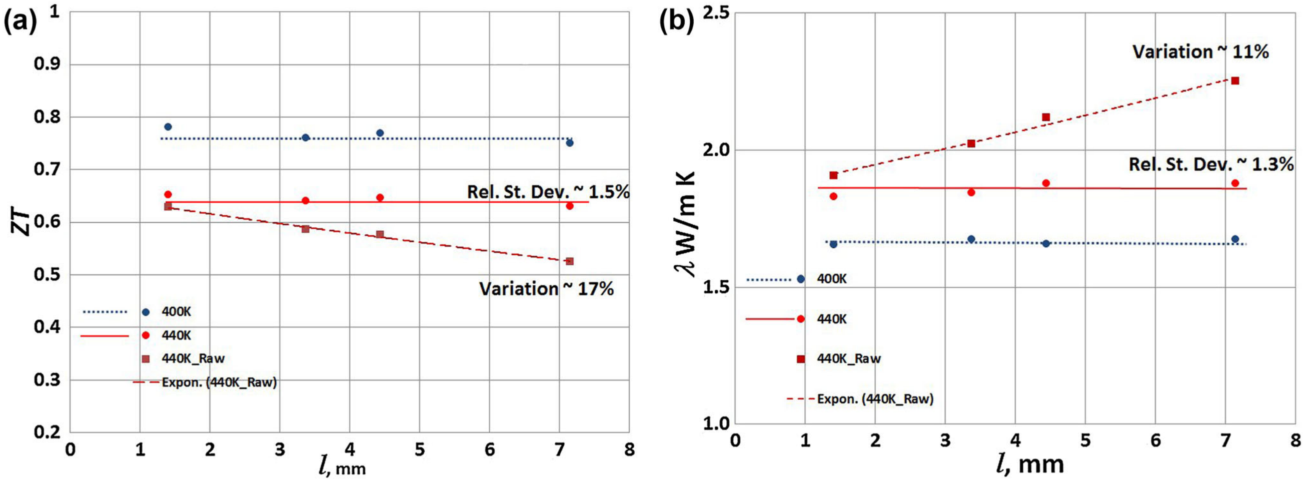

Fig. 4. Raw (at 440 K, solid squares) and 2SSC corrected (at 440 K and 400 K, solid circles) values of ZT (a) and λ (b) measured on four samples with lengths of 7.15 mm, 4.44 mm, 3.75 mm, and 1.41 mm.

1% of each other (irrelevant of the temperature increment) all samples with different lengths were later characterized using only the runs with a 15 K step increment as this is less time-consuming.

As pointed out in our earlier publications,[12,13] only ZT and λ values need to be corrected to take into account thermal losses. Figure 3 shows the temperature variation of ZT (a) and of the thermal conductivity (b) for the longest sample, which is the one subjected to the largest correction by these parasitic phenomena. Dashed curves show uncorrected (raw) data for comparison. As expected, the difference between raw and corrected data increases with temperature reaching about 18% at 440 K for both properties. The two sample system calibration (2SSC) automatically employed by the ZT-Scanner during the measurement generates corrected values by taking account of the temperature and geometry of the sample.

Figure 4 shows values of the figure of merit and of the thermal conductivity delivered by the ZT-Scanner at two temperatures, 400 K and 440 K and presented as a function of their length. The raw data at 440 K is also shown. Since the thermal exchange between the sample and its environment increases with temperature the highest temperature (440 K) is the one showing the largest correction and was chosen for the analysis.

It is clear from Fig. 4 that the corrected values of both the figure of merit and of the thermal conductivity are very close for these samples whose length varies by up to a factor of 5; indeed the standard deviations do not exceed 1.5%. Also, note that variations of the raw data for the same experiment are about 17% for ZT and 11% for λ from the shortest up to the longest sample. In Ref. 5, we recommended a sample length from 4 mm to 7 mm for optimal ZT-Scanner measurements. However, further measurements, as shown in Fig. 4, demonstrate the reliability of the 2SSC procedure for samples whose length goes down to 1.4 mm, which helps to remove an important limitation, as mentioned in the introduction.

It is also important to note that the value of 1.41 mm for sample length does not represent a fundamental limitation, but a technical one. When soldering thinner samples between the contact plates a special tool is required. It is well known from experience in TE module manufacturing how difficult it becomes to make low resistivity contact for the short-legged modules. Further shortening of the sample will definitely create a similar difficulty. A minimum sample length of about 1 mm looks as a reasonable compromise for most practical situations.

Other known systems for TE characterization presently available on the market require a sample size of 10 mm diameter and 5 mm height for ZT-Meter870K[17] (Fraunhofer Institute of Physical Measurements), a prism or cylindrical form from 6 mm to 22 mm long for Seebeck coefficient/electric resistivity meter ZEM-3[18] (Ulvac-Riko) and for LSR-3[19] (LINSEIS), and a disc diameter from 12.7 mm to 25.4 mm for SBA 458 Nemesis[20] (Netzsch). Only the ZT-Meter870K is designed to measure all parameters on one sample. ZEM-3 characterization has to be further complemented with Laser flush thermal diffusivity meters such as Netzsch LFA 457, Linseis LFA-1000 with another disc shaped sample from 10 mm to 25 mm in diameter. SBA 458 Nemesis and LSR-R are able to measure thermal diffusivity on the same disc; however, they do not respect the same direction as for the electrical resistivity and Seebeck coefficient. Therefore none of these systems can measure the main four TE parameters on one sample as small as it was demonstrated for the ZT-Scanner.

CONCLUSIONS

In this study, we confirmed that the main thermoelectric parameters such as the figure of merit, electrical conductivity, Seebeck coefficient, and thermal conductivity can be accurately assessed on a sample sized down to $4 \times 4 \times 1.4\ \mathrm{mm}^3$ whose volume is about two orders of magnitude smaller than that required by the specimens in Refs. 8–11 needed for separate measurements. This size translates in roughly <100 mg in weight for most TE alloys. Our results were obtained on a well-studied bismuth telluride based material which was selected for its homogeneity thus increasing both reliability and accuracy. However, they are expected to be valid for the full TE characterization of any unknown material to which one can provide a satisfactory electric and thermal contact, because the 2SSC procedure not only accounts for variations of sample geometry, but also for sample composition explicitly through their thermal conductivities.[12] These results indicate that the ZT-Scanner allows to radically decrease specimen sizes which has the potential to significantly accelerate the investigation of novel TE materials which will be needed for large scale waste heat recovery.

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