Journal of ELECTRONIC MATERIALS, Vol. 45, No. 3, 2016
DOI: 10.1007/s11664-015-4101-1
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Consistency of ZT-Scanner for Thermoelectric Measurements from 300 K to 700 K: A Comparative Analysis Using $Si_{80}Ge_{20}$ Polycrystalline Alloys

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A Harman-based instrument for the characterization of thermoelectric (TE) materials in a wide temperature range (the ZT-Scanner) was introduced in an earlier publication, with a focus on a two-sample system calibration (2SSC) procedure used for the precise evaluation of thermal losses during the measurements. This technique offers an option to accurately measure the main TE parameters from 300 K to 700 K. We now report the results of ZT-Scanner measurements of *p*-type $Si_{80}Ge_{20}$ polycrystalline samples, including the TE figure of merit *ZT*, Seebeck coefficient, and thermal and electrical conductivities. These samples proved to be extremely stable up to the maximum temperature of measurement, and could eventually serve as a standard for thermoelectric characterization. The measurements were performed using both PbSn solder and conductive silver paste contacts. In all cases, Ni plating was used as a protective barrier between the TE alloys and the contact material. The experimental data has been compared to the typical data measured by the Jet Propulsion Laboratory on similar samples, providing a quantitative estimation of the accuracy of the measurement system, which has been found to be better than 0.015, or 5%, up to 700 K for *ZT*. The consistency of the TE measurements is evaluated by means of a statistical analysis of repetitive tests on the same and on different samples of identical nature. We also analyze the influence of thermal and electrical contact resistance on the measured properties.

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

INTRODUCTION

After decades of continuous progress in thermoelectricity, the applied metrology in this area of research and development remains a concern. Reliable thermoelectric (TE) measurements to characterize materials and devices are essential to advance knowledge and practical applications, such as, for example, the improvement of TE performance of novel materials. Unfortunately, despite continuous efforts, the precision and accuracy in the evaluation of the dimensionless TE figure of merit *ZT* (*T* is the temperature in Kelvin, and $Z = \alpha^2/\rho\lambda$ where α, ρ and λ are, respectively, the Seebeck coefficient, the electrical resistivity and the thermal conductivity) are not yet satisfactory;[1–11] in particular there are no standards provided by national laboratories on metrology. A recent publication[12] introduced the ZT-Scanner (TEMTE Inc.), a new Harman-based system,[1,2,8] which, when it is combined with a two-sample calibration procedure

(Received June 3, 2015; accepted September 28, 2015; published online October 15, 2015)

(2SSC), provides reliable measurements of ZT α, ρ and λ from 300 K to 700 K. A significant advantage of a Harman-based setup is its capability to provide the simultaneous measurement of all TE parameters on one sample and one single temperature run. This ability eliminates the potential for additional errors that may be introduced in conventional ZT evaluation when α, ρ and λ are measured separately on physically different samples.[6,7] The analysis of the 2SSC procedure presented in[12] indicated this instrument's precision to be at about 1% of measured values; however, we perceived that further experimental evaluation of its precision and accuracy are still needed to support consistency of measurements with ZT-Scanner, which is the purpose of this paper.

In the present study, the evaluation of a 0.2% (or better) precision at room temperature was assessed via repeated measurements of one p-type sample with a bismuth-telluride-based composition,[13–15] suitable for temperatures near 300 K. For precision and accuracy at elevated temperatures, we used p-type $Si_{80}Ge_{20}$ polycrystalline samples, which have shown high thermocyclic stability[16] up to 800 K and could eventually serve as a standard for thermoelectric characterization. These samples were generously provided, together with a temperature-resolved set of parameters by the Jet Propulsion Laboratory (JPL). Through a series of repeated tests on these samples and a statistical analysis of the measurements, we confirm accuracy of 5% (or better), up to 700 K, for ZT values.

EXPERIMENTAL

All the tests reported in the present study were carried out on the development version of the ZT-Scanner (TEMTE Inc.), which differs from the commercial version only in its less compact design with easier access to the system components; it employs the same software, TE Properties. The calibration procedure for Harman-based system is established in Ref. 12. A sample mounted in a two-point contact setup is sandwiched between two copper contact plates and placed on the top of a copper sample holder, where it is covered (without physical contact) by an aluminum thermal shield. The ZT-Scanner implements a bipolar Harman procedure[8] to compensate the influence of Joule heating on ZT measurements. The temperature of the sample can be varied from 300 K up to 720 K. Measurements are performed under vacuum with a residual pressure lower than 3×10^{-3} Torr to minimize thermal exchange between the sample and its environment. A more detailed description of the ZT-Scanner and the 2SSC can be found in Ref. 12.

The direct current (DC) circulating through the sample during a Harman test was always set at a 100 mA. The stabilization time for each of the four phases of the Harman procedure was 5 min. Increments of 15 K or 20 K were used in temperature-resolved measurements with 40 min stabilization time between each temperature step.

Four samples were used in this study. For room temperature tests, a p-type bismuth-telluride-based sample in a rectangular parallelepiped shape (6 mm $\times$ 5 mm $\times$ 5 mm) was cut from a rod of an alloy synthesized by hot extrusion. This material is one of the most frequently used alloys for modules operating near room temperature. The direction of the DC current during the measurements is parallel to the extrusion axis and to the longer side of the sample. For the measurements with repetitive heating, we used p-type $Si_{80}Ge_{20}$ polycrystalline samples. These samples with initial size of 18 mm $\times$ 2.72 mm $\times$ 6.5 mm were provided by the JPL. We used three different samples (#1, #2 and #3 in text below) from the same lot, which were reduced with a dicing saw to the length of 6.7 mm to fit the recommended size range of the ZT-Scanner.[12] The electric current during a Harman test is parallel to the longest side. Both types of samples were contacted via an electroplated Ni deposit of about 3 μm. One-component conductive silver paste was used to mount $Si_{80}Ge_{20}$ sample #1 on the contact plates for measurements. Bismuth-telluride-based sample and $Si_{80}Ge_{20}$ samples #2 and #3 were attached to the copper contact plates by soldering with a PbSn alloy. Soldering time was reduced to less than 20 s to avoid inter-diffusion between Ni and PbSn.

RESULTS AND DISCUSSION

Influence of the Electrical Contact Resistance on Harman-based Measurements

It is common knowledge that excessive resistivity of electrical contacts may cause problems in two-point contact measurements, which are usually employed in Harman-based systems.[12,17] In Ref. 12, we reported that the contact resistivity can be as low as 6×10^{-7} Ωcm^2 when PbSn soldered contacts are applied over electroplated Ni, while we obtained 7×10^{-6} Ωcm^2 for contacts with silver paste over Ni. Such low values ensure accurate measurements for most TE materials; however, it should not be discarded that optimal contact options with lower resistivity can yet be found. Therefore, we have studied the influence of contacts with higher resistivity on Harman-based measurements. The $Si_{80}Ge_{20}$ sample #1 with silver paste contacts without high temperature paste curing[12] was used for this purpose. Its effective electrical resistivity before curing, calculated as $\rho_{eff} = R_m \times A/l$ (where R_m is measured sample resistance, and A, l are the cross-section and length of sample), was about 40 $\mu\Omega$m at room temperature. The dashed lines on Fig. 1a and b respectively show the variations of ZT and ρ_{eff} values as a function of the "curing" temperature run #1. The sharp increase of the TE figure of merit between 380 K and 480 K perfectly correlates with the decrease of ρ_{eff}, and corresponds to progressive curing of the silver paste contact. Temperature run

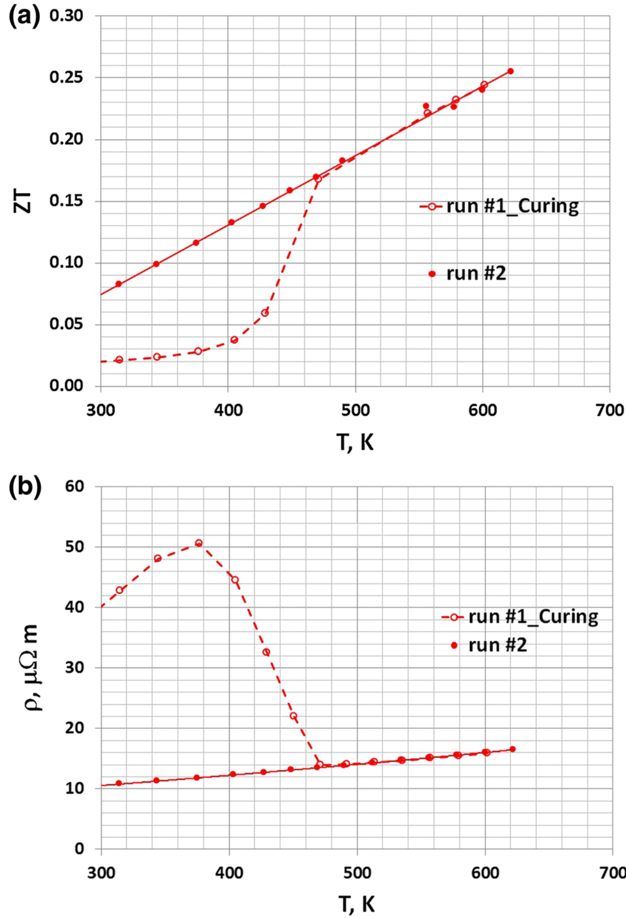

Fig. 1. Temperature variations of ZT (a) and ρ (b) values for $Si_{80}Ge_{20}$ sample #1. Dashed line and open circles correspond to the first temperature run (run #1), which cures the silver paste contact. Solid line and solid circles correspond to the following run, (run #2), with fully cured contacts.

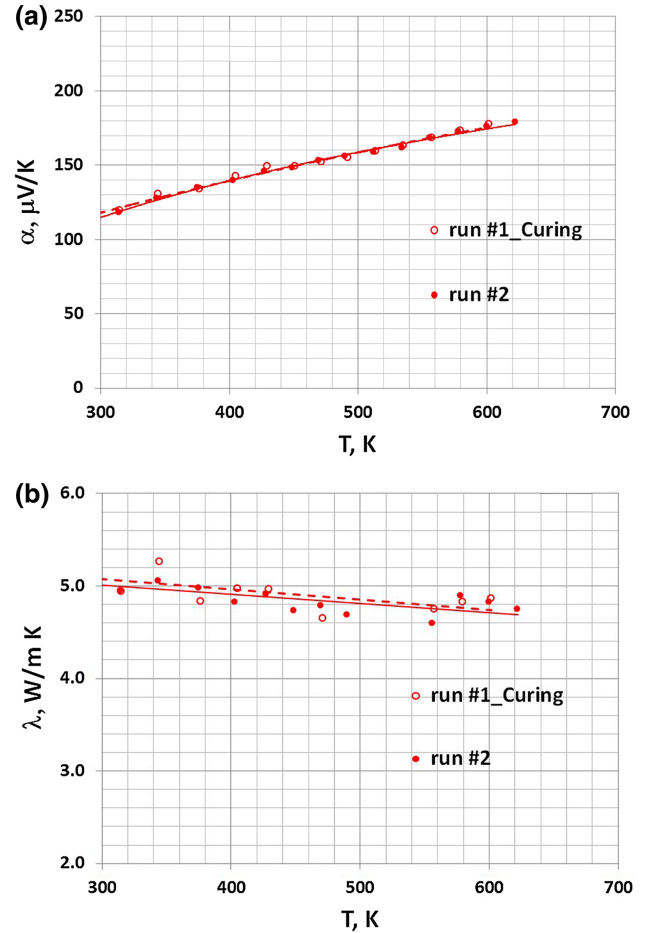

Fig. 2. Temperature variations of the Seebeck coefficient α (a) and of the thermal conductivity λ (b) values for the same $Si_{80}Ge_{20}$ sample#1 of Fig. 1. Dashed line and open circles correspond to the first temperature run, which cures the silver paste contact. Solid line and solid circles show the results of the following run #2 with fully cured contacts.

#2, shown on both Fig. 1a and b by solid lines (and circles), represents the real performance of this $Si_{80}Ge_{20}$ sample, because the contact resistivity is now lower, giving a room temperature value of the sample resistivity ρ of 10.5 $\mu\Omega$m. Figure 2a and b respectively show the Seebeck coefficient and the thermal conductivity of the same sample measured simultaneously with ZT and ρ during both runs. Comparison of the data of Fig. 1 shows how misleading the ZT and ρ data obtained with high resistivity contacts can be for temperatures lower than 480 K; however, as it follows from Fig. 2, the Seebeck coefficient and thermal conductivity data for both runs, with high and low resistivity contacts, show almost identical data.

This means that, even if the measurements are performed with poor contacts, a Harman-based system is still able to deliver valuable information. This is indeed the case for the Seebeck coefficient, because it is measured with open circuit and fundamentally not influenced by contact resistivity. For the thermal conductivity measurements, the situation may not be so simple. Its value is calculated as $\lambda_m = \alpha^2/(Z_m \times \rho_m)$, and may still be equal to the real thermal conductivity λ of the material only in the case when $(Z_m \times \rho_m) = (Z \times \rho)$ even if $Z_m \neq Z$ and $\rho_m \neq \rho$, which would be the case when the imperfection of the contact is simply due to its higher electrical resistivity. Fortunately, for most thermoelectric materials, this is the case. High performance TE materials usually possess very high electrical conductivity and a low thermal conductivity.[17] This means that the impact of a contact with limited electrical conductivity is different for electric and thermal measurements. Excessive resistivity greatly affects the measured ρ_m value, while it only marginally affects the thermal conductivity. Figure 3 shows that the product $(Z_m \cdot \rho_m)$ is not influenced by poor contact quality in the whole temperature range, which explains, as predicted, the reproducibility of λ measurements.

Precision of Measurements with ZT-Scanner

The precision of the ZT-Scanner measurements was evaluated using different samples and different contact options. Table I shows the results of 14 consecutive measurements of one *p*-type bismuth-telluride-based sample, which is suitable for room temperature tests. The sample was contacted with electroplated Ni, followed by PbSn soldered alloy. All measurements were performed at room temperature without opening the vacuum chamber and reinstalling the sample.

As can be seen from Table I, the relative standard deviation for all measured parameters is lower than 0.2%, which shows both the high reproducibility and the precision of measurements at room temperature.

We have chosen a stable *p*-type $Si_{80}Ge_{20}$ sample to evaluate the precision of the ZT-Scanner measurements when the temperature varies. Temperature runs were carried out from 300 K to 450 K on $Si_{80}Ge_{20}$ sample #2 with electroplated Ni and PbSn soldered contacts.

Figure 4 shows results of ten consecutive temperature-resolved measurements of the TE figure of merit (a), electrical resistivity (b), Seebeck coefficient (c) and thermal conductivity (d).

In order to evaluate the precision of measurements in this temperature range, we have chosen four fixed temperature values, and evaluated the measured properties at these temperatures using the best-fit lines through the data shown in Fig. 4. Figure 5 represents ZT (a), ρ (b), α (c) and λ (d) at 300 K, 350 K, 400 K and 450 K calculated from the tendency lines of the individual temperature runs (Fig. 4). These results show a systematical decrease of ZT and increase of ρ, with a rate of about 0.8–0.9% per each temperature run. However, both α and λ demonstrate only statistical variations around their average values for each temperature. At 300 K, the relative standard deviation is 0.2% for α and 0.6% for λ, increasing to 0.5% and 1.1%, respectively, at 450 K.

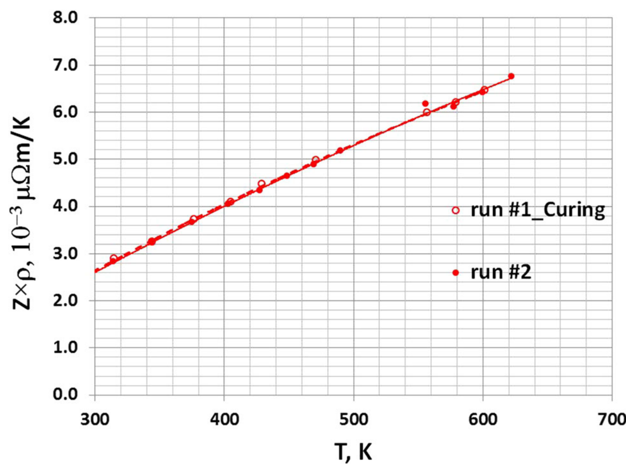

Fig. 3. Variations of the product ($Z_m \times \rho_m$) values as a function of temperature for the same $Si_{80}Ge_{20}$ sample #1 of Figs. 1 and 2, for the two consecutive runs. Dashed line corresponds to the first temperature run, which cures the silver paste contact. Solid line shows run #2 with fully cured contacts.

We interpret the systematical variation of ZT and ρ as being the result of inter-diffusion of Ni and PbSn soldering alloy with repetitive heating. This diffusion probably leads to an increase of the contact resistivity. Figure 6 shows the statistical variation of the product ($Z_m \times \rho_m$) at these four chosen temperatures as it evolves during successive measurements with a relative standard deviation equal to 0.2%, which confirms our assumption. As we discussed in "Influence of the Electrical Contact Resistance on Harman-based Measurements" section α and λ values are not influenced by the variability of the contact electrical resistivity.

Data in Table I and Figs. 4, 5, and 6 were obtained by repeating measurements on samples that were mounted only once; and thus, any possible influence of human error was excluded. Under these circumstances, a high degree of precision of these measurements was found. No repetitive tests of the instrument with Ni and silver paste contacts will be shown here, since Ni plating and silver paste applying/curing has to be redone by an operator between the tests, which involves human intervention.

Accuracy of TE Measurements with ZT-Scanner

With respect to a measurement of a physical quantity, the accuracy refers to how close the measured value is to the true value of that quantity, whenever it may be assumed that the property being measured possesses a known true value. Extending this notion to evaluate the accuracy of a measurement system then requires to establish a comparison of the results produced by the system with known values, or standards of measurements, accepted as true values. In thermoelectricity, establishing these accepted standards remains an unsolved problem for the community. For instance,

Table I. Statistical analysis of 14 consecutive measurements by ZT-Scanner of a BiTe-based sample

Value	T (K)	α (μV/K)	ρ ($\mu\Omega$m)	λ, [W/(m K)]	Z (10^{-3} K^{-1})	ZT
Mean	289.86	192.76	7.964	1.755	2.658	0.770
St. dev.	0.05	0.21	0.005	0.003	0.001	0.0004
Rel. st. dev. (%)	0.018	0.11	0.062	0.19	0.047	0.051

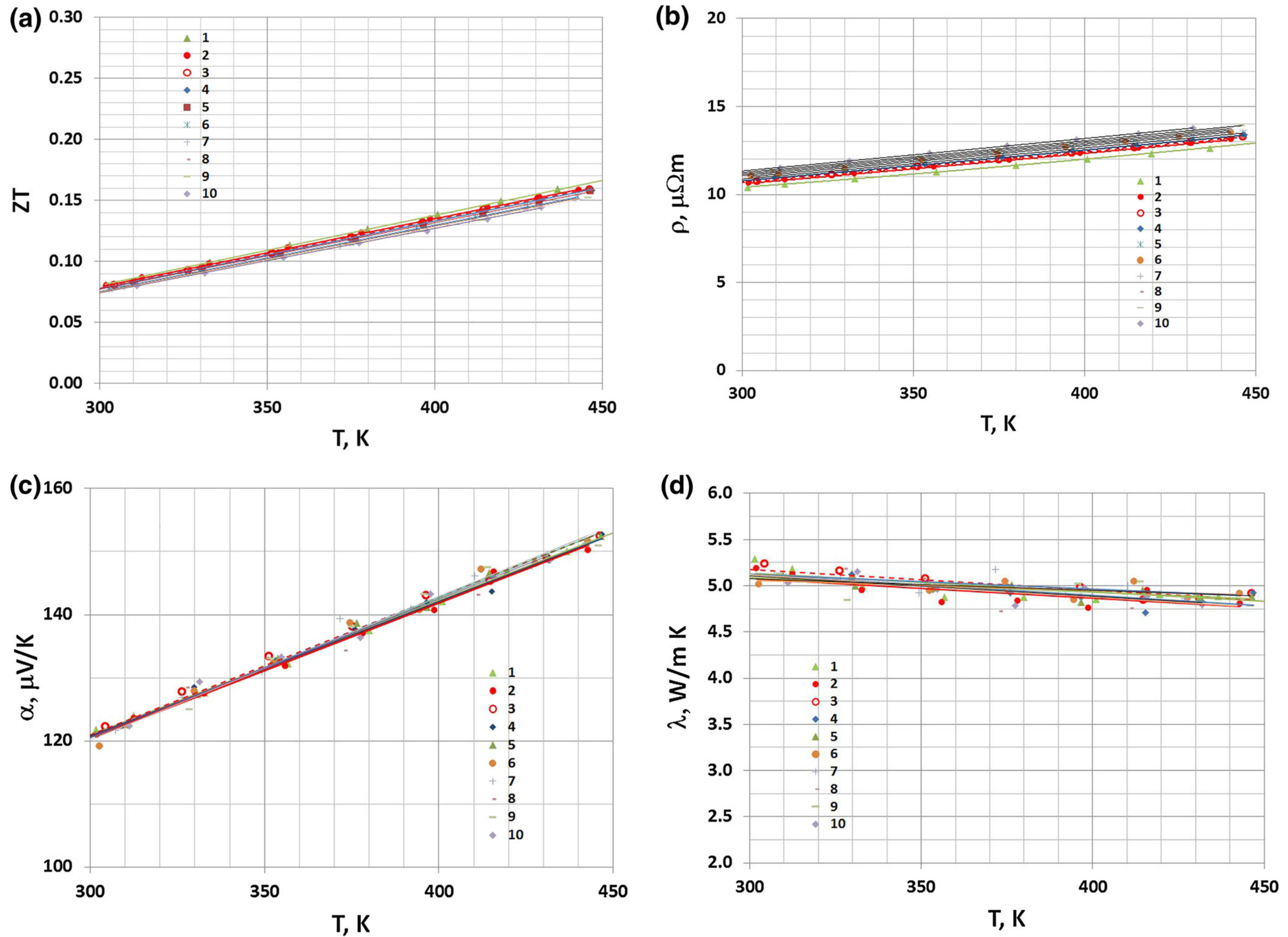

Fig. 4. Results of ten consecutive temperature runs with simultaneous measurements of *ZT* (a), ρ (b), α (c) and λ (d) measured on one $Si_{80}Ge_{20}$ *p*-type, sample #2, with electroplated Ni and PbSn soldered contacts.

the US National Institute of Standard and Technology (NIST), or a similar organization of any other country, does not provide the standard samples with the set of all thermoelectric parameters of interest, not even for one specific temperature. In order to assess the accuracy of the ZT-Scanner, we have herein used the best possible option, which is to choose as a standard material a polycrystalline $Si_{80}Ge_{20}$ alloy, which has already been proven as very stable in measurement cycles up to 800 K.[16] These samples were provided for this study, together with a temperature-resolved set of parameters, by the JPL. Figure 7 shows the temperature variations of *ZT* (a), ρ (b), α (c) and λ (d) values, which were measured on three different SiGe samples. Sample #1 was mounted on the system using Ni and silver paste contact, whose measurements were presented in "Influence of the Electrical Contact Resistance on Harman-based Measurements" section. Samples #2 and #3 were mounted with Ni and PbSn soldered alloy.

In Fig. 7, we also show two types of tendency lines: 1) solid red lines, which combine experimental data acquired by the ZT-Scanner on all three samples; and 2) blue dashed lines, which represent standard data supplied by JPL for this type of samples. The highest observed discrepancies between tendency lines are: 0.015 or 5% for the *ZT* value at 700 K; 5 μV/K or 4% for α at 300 K decreasing to near zero from 500 K to 700 K; 0.1 W/m K or 2% for λ from 300 K to 700 K; 1 $\mu\Omega$m or 8% for ρ from 300 K to 700 K.

The largest difference between the two sets of data is observed for the electrical resistivity. Interestingly, the ρ values measured by the ZT-Scanner with a two-point contact method are lower than those of the reference data, which rules out the possibility of error induced by the contribution of the electrical resistivity of the contacts. We explain the difference in ρ values by the difference in the experimental methods of resistivity measurement. The reference data were collected using the van der Pauw method, for which the current lines are usually more complex than for a two-point setup on a rectangular parallelepiped sample. This method has the advantage of a four-point contact approach used

Fig. 5. Variation of *ZT* (a), ρ (b), α (c) and λ (d) obtained from the tendency lines at each one of the four chosen fixed temperatures as a function of the test number measured on one *p*-type $Si_{80}Ge_{20}$, sample #2, with electroplated Ni and PbSn soldered contacts.

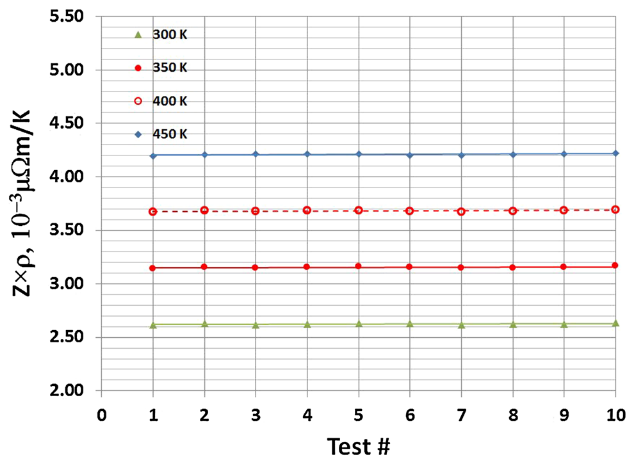

Fig. 6. Variation of the product ($Z_m \times \rho_m$) at the four chosen fixed temperatures as a function of the test number measured on *p*-type $Si_{80}Ge_{20}$ sample #2 with electroplated Ni and PbSn soldered contacts.

to avoid the unwanted impact of contact resistance, but in exchange, it requires truly dimensionless point contacts for extreme accuracy.[18]

CONCLUSIONS

The ability to efficiently and accurately characterize the TE performance of synthesized samples is an essential component for the development and subsequent improvement of novel TE materials. The Harman approach has the advantage that it simultaneously measures properties of the same sample that are closely related to the material performance in devices, and as such, the measurements are more relevant than those obtained by other methods or combination of methods. The developed Harman-based system has been used for that purpose for many years at Polytechnique Montreal. However, it is only after the successful implementation of a 2SSC calibration procedure[12] that we have obtained consistent and accurate measurements of *ZT*, ρ, α and λ in a large temperature interval from room temperature up to 720 K, and on samples of different material compositions.

The 2SSC procedure solves the problem of variability of the *ZT* and λ correction factors with respect to variations in sample geometry and composition. In some instances, however, the samples may be thinner than required for optimal

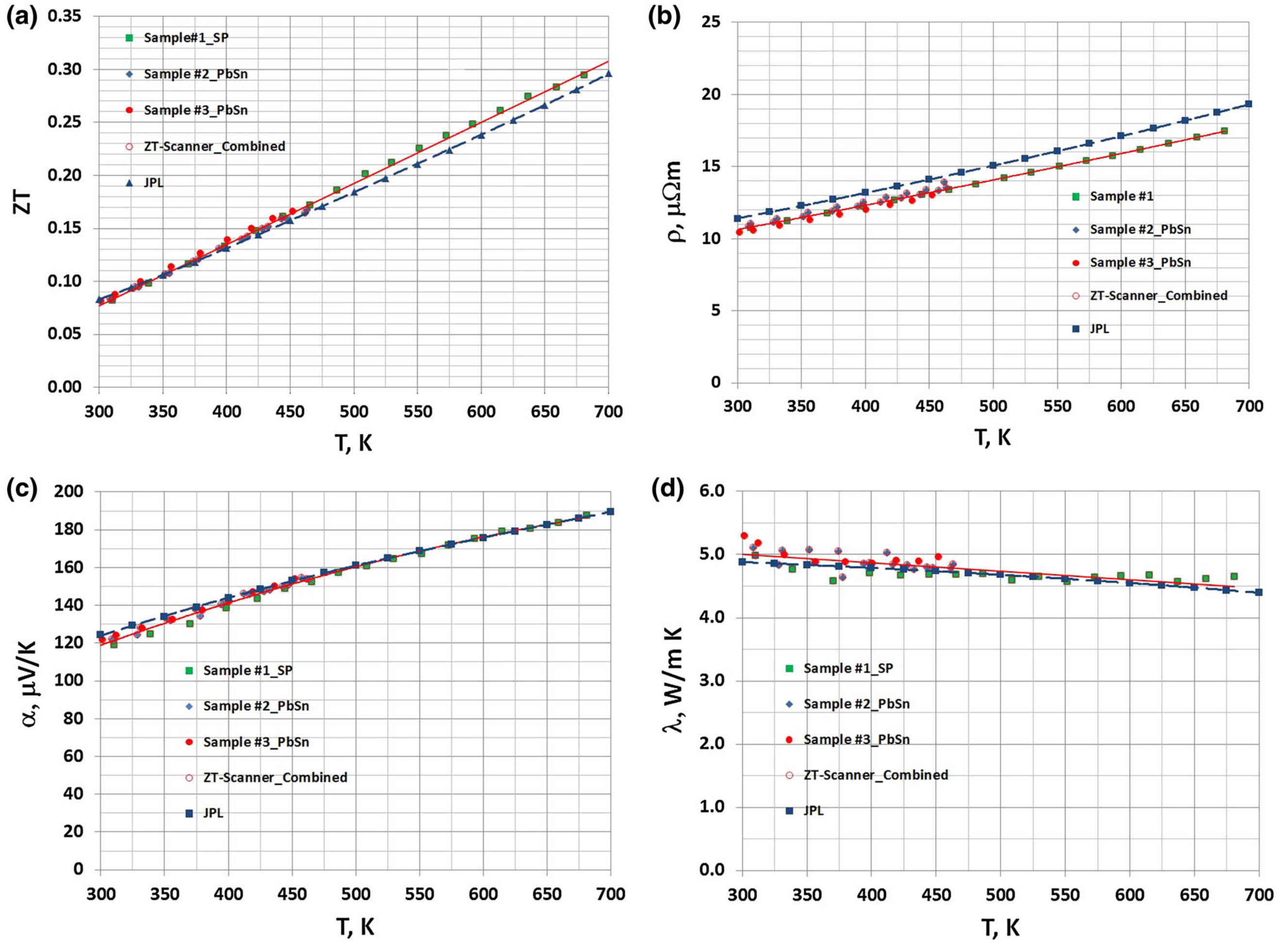

Fig. 7. Variations of ZT (a), ρ (b), α (c) and λ (d) values with temperature measured by the ZT-Scanner on three different $Si_{80}Ge_{20}$ samples. Blue dashed lines show standard JPL data for this type of samples and red solid lines combine experimental data acquired on all three samples.

measurements, leading to an unfavorable ratio of TE material and contact resistances. In such cases, we recommend the use of the more reliable $(Z_m \times \rho_m)T$ product value instead of ZT to evaluate the TE performance.

The present study shows that the precision of the measurements provided by the ZT-Scanner is better than 0.2% at room temperature for ZT, ρ, α and λ values. Results presented here for consecutive temperature runs from 300 K to 450 K for a $Si_{80}Ge_{20}$ sample show a relative standard deviation at 300 K of 0.2% for α and 0.6% for λ, which respectively increase to 0.5% and 1.1% at 450 K. A systematic variation of ZT and ρ with test repetition, covering this temperature interval, was observed on this $Si_{80}Ge_{20}$ sample, probably as a result of inter-diffusion of Ni and PbSn soldering alloy. If our assumption is correct, then we expect the relative standard deviation for ZT and ρ to be better than 0.2% for the first temperature run, similar to the room temperature measurements, because there would be no major influence of diffusion. The numbers for instrument's precision, which we report here, are in the good agreement with those that we estimated in Ref. 12.

The accuracy of this system was estimated by comparison with JPL standard data, and it has been found to be better than 0.015, or 5%, up to 700 K for ZT values; 5 μV/K, or 4%, for α at 300 K decreasing to near zero from 500 K to 700 K; 0.1 W/m K, or 2%, for λ from 300 K to 700 K; 1 μWm, or 8%, for ρ from 300 K to 700 K. Given that the resistivity values were lower than the standard data, ruling out any adverse effect of contact resistance, the accuracy of ρ measurements is probably better than 8%, but this remains to be confirmed by additional testing of the electrical resistivity by a variety of other methods.

We believe that all the values reported here signal clear progress in this field, and they support the consistency of TE measurements provided by the ZT-Scanner instrument from 300 K to 700 K. Further analysis of accuracy still requires a set of well-established stable standard samples.

ACKNOWLEDGEMENTS

We acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC), the infrastructure support provided by the Régroupement Québecois sur les Matériaux de Pointe, and of the Fonds de Recherche du Québec - Nature et Technologies (FRQNT), Projet de Recherche Orientée en Partenariat. Part of this work was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

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