The International Thermoelectric Society

SCT- 93

SHORT COURSE ON THERMOELECTRICS

FOR THE GREEN
21st CENTURY

Pacific Convention Plaza Yokohama
Japan

8th November 1993

Sponsored by the International Thermoelectric Society
Organized by ITS Japan Branch
Short Course on Thermoelectrics - 1993 (SCT-93)
Organized by: The International Thermoelectric Society (ITS)
ITS Japan Branch
c/o K. I. Uemura
2-14-21, Yokodai, Isogo-ku, Yokohama-shi,
Kanagawa-ken, 235 Japan
Tel:(81)45-832-1888, Fax:(81)45-832-8208

Cover design by Masami Ishii, copyrights on the Nihon Keizai Shimbun.
CHARACTERIZATION OF
TE MATERIALS AND DEVICES

Richard J. Buist

TE TECHNOLOGY, INC.

1. INTRODUCTION

This paper is a review of the problems and solutions related to the testing and characterization of thermoelectric (TE) materials and devices. By comparison, TE devices are relatively simple to test. They involve the use of standard laboratory equipment for sensing voltages and temperatures. One needs only to carefully follow typical laboratory procedure for setting up a thermal and electrical performance test and extracting the data of interest. Generous application of temperature sensors will at least identify experimental problem areas which can subsequently be corrected.

The problems associated with accurately extracting TE material data are much more difficult. In fact, the measurement technology employed by many researchers today is not very consistent with the world growth of high-technology capabilities. This has fostered many questions regarding reproducibility and test agreement between various sources who use different means of obtaining data.

These fundamental problems are addressed herein. Also, a new method is introduced for obtaining accurate test data on TE materials which is also usable for testing TE devices as well. Although only applicable to materials with a "reasonably good" TE Figure of Merit, this method could become the standard in the entire TE industry for testing and characterizing TE materials and devices.

2. TE MATERIAL PARAMETERS

The performance of a thermoelectric (TE) device is governed by the following material parameters:

Seebeck coefficient, $\alpha$
Electrical resistivity, $\rho$
Thermal conductivity, $\kappa$.

These parameters and how they vary with temperature throughout the operating envelope are essential to quantify for one who wishes to develop TE materials or design and analyze TE devices.

There is still a lot of confusion in the TE industry over the Figure of Merit, $Z$. Some TE material researchers have equated $Z$ to the
measurement of the maximum temperature differential, ΔT_{max}, that a
TE device can produce from a constant (infinite) heat sink
temperature. However, this is categorically not true. That
"infamous" expression was derived assuming that each TE material
parameter was constant with temperature. The proliferation of high-
speed personal computers certainly nullifies the need for this
simplifying assumption.

The Figure of Merit, Z, is a **material** parameter defined by the
formula given in equation (1):

\[
Z = \frac{\alpha^2}{\rho \kappa}
\]  

Since \( \alpha, \rho \) and \( \kappa \) are each variable with temperature, there can be no
single value of \( Z \) that equates to a device parameter such as \( \Delta T_{\text{max}} \).
\( Z \) values inferred from \( \Delta T_{\text{max}} \) tests, are quite ambiguous and should
not be considered as a substitute for \( Z \) as defined in the above
equation. Certainly, \( \Delta T_{\text{max}} \) is a very important parameter and is
probably the most indisputable verification of the worthiness of a
TE material from the performance standpoint, but it is impossible to
infer a \( Z \) value from this measurement without knowing the
temperature dependence of all of the TE material parameters.

Certain measurement techniques provide for the direct measurement of
this parameter. Therefore, \( Z \) will be considered as a fourth
material parameter of interest, even though there still remains only
three independent TE material parameters. Measurements of any three
TE material parameters will yield the data needed to characterize
the performance of devices made therefrom.

The following is a discussion of these "four" parameters and the
problems associated with obtaining accurate measurements of each.

### 2.1 Seebeck Coefficient, \( \alpha \)

The measurement of \( \alpha \) is determinable using the following formula,
representing its definition:

\[
\alpha = \frac{V_o}{\Delta T}
\]

Where:

- \( V_o \) = Open circuit voltage produced by \( \Delta T \).
- \( \Delta T = T_h - T_C \)
- \( T_h \) = Temperature of hot point on the TE material.
- \( T_C \) = Temperature of cold point on the TE material.

This looks like a very simple expression and, on the surface, this
appears to be a relatively easy measurement. However, upon
installing the probes needed to test \( V_o \), the following equation
better describes the experimental setup:
\[ V_w = \alpha \Delta T + \alpha_w \Delta T \]  \hspace{1cm} (3)

Where:

- \( V_w \) = Measured open circuit voltage produced by \( \Delta T \).
- \( \alpha_w \) = Seebeck coefficient of the voltage probe wires.

In order to determine the true \( V_o \), one would need voltage probes with zero Seebeck coefficient (\( \alpha_w = 0 \)). Alternatively, it would be necessary to know the Seebeck coefficient of the measuring probes at \( T_h \) and \( T_c \), and insert this value into equation (3).

The second problem in measuring \( \alpha \) is to accurately measure the temperatures \( T_h \) and \( T_c \) at the **exact point** where the voltage probes make contact with the TE material. Imperfect thermal contact by the temperature sensors and thermal gradients in the sensor leads must be accounted for to assure precision. Also, since the accuracy of this measurement is dependent on the temperature differential, \( \Delta T \), the temperature sensors should be as equivalent as possible and provide for the necessary resolution and stability. The best way to test this parameter is to use a method whereby the specimen can be thermally reversed. This way, the average of the two, bi-polar test results will correct for most effects which may cause unbalance of the temperature sensors.

### 2.2 Electrical Resistivity, \( \rho \)

The measurement of \( \rho \) is determinable from a regular shaped TE pellet specimen using the following formula, representing its definition:

\[ \rho = \frac{V_r A}{IL} \]  \hspace{1cm} (4)

Where:

- \( I \) = Applied current through the material.
- \( V_r \) = Voltage produced solely due to the applied current, i.e., the resistive component of voltage.
- \( L \) = Dimension of the TE material sample in the direction of the current flow.
- \( A \) = Cross-sectional area of the TE material.

The measurement of \( \rho \) also has its problems. The value, \( V_r \), as defined, is not easily measured. Application of a DC current, \( I \), through a regular-shaped TE pellet yields the following voltage:

\[ V_i = V_r + V_o + V_c \]  \hspace{1cm} (5)

Where:

- \( V_c \) = Voltage due to electrical contact resistance.
- \( V_i \) = Measured voltage under and applied DC current, \( I \).
The value of $V_C$ can be dealt with by one of two means: (1) Use separate voltage probes directly onto the TE sample "inside" the electrical contacts (4-probe method) or (2) either accurately determine $V_C$ or reduce it to such a low value that it can be neglected (2-probe method). See sections 4.2 and 4.3 below.

Separating, $V_O$ from $V_R$ is also not easy. The most common method is to use an alternating current (AC) which instantaneously reverses $V_R$ but not $V_O$ since it is not directly dependent on applied current. However, commercial AC resistance meters which use the standard sinusoidal wave-form are not dependable for thermoelectrics. Peltier heat pumping is instantaneous with applied current resulting in a sinusoidal heat pumping waveform not in phase with the slower Joule and thermal conduction effects. This very complicated thermal situation can seriously affect the accuracy of the readings. One can prove this to himself by simply monitoring the "AC-resistance" of a TE device using a commercial AC resistance meter and quickly heat one surface with a lighted match. An anomalous transient AC resistance reading will be clearly evident, not explainable from the temperature dependence of TE device resistance.

There are some commercial AC resistance meters which employ a bipolar square wave as the current source. This is better, but it still has some fundamental problems affecting accuracy. That is, the Peltier effect is still operable during the half-cycle of applied current and this voltage does, indeed, rise during each on-cycle. A typical TE pellet of 1.14 mm long has a time constant of less than one second. This means that, at the typically applied current frequency of 40 Hz, the voltage will rise as much as 5% during each half cycle due to the Seebeck voltage generated by the Peltier effect operating during each half-cycle. This introduces corresponding errors in the measurement of $V_R$. Higher frequencies will lower this error but will create other errors in the voltage measurement due to inductance in the circuit.

Finally, it will be very important to know the temperature dependence of $\rho$ in order to evaluate the material for its TE performance. Therefore, the $\rho$ measurement technology must include provisions for measuring the temperature of the specimen during the measurement of its electrical parameters.

### 2.3 Thermal Conductivity, $\kappa$

By far, the most difficult TE material parameter to measure is the thermal conductivity, $\kappa$. It is defined by the following equation:

$$\kappa = \frac{Q L}{A \Delta T}$$  \hspace{1cm} (6)

Where:

$Q =$ Heat flow through the material between the points defined by $\Delta T$.  

4
The problems associated with accurately measuring ΔT were discussed earlier in section 2.1. Also, thermal contact resistance can exist at the specimen boundaries creating a situation very similar to that as described for electrical contact resistance discussed in section 2.2. The solutions to these two problems are also the same as those described above.

The primary reason why κ measurements are so difficult is that the measurement of Q is very difficult to determine. If a heater is used to create a heat source, some of its heat will flow into the environment as well as through the TE specimen. "Relative" measurements are often used by sandwiching a "known" standard in series with the specimen and measuring the temperature gradient within it to "calibrate" the heat flow. This method makes the accuracy of the result dependent on the accuracy of the standard, which may be questionable itself. In any case, this technique does not preclude the ΔT measurement and thermal contact resistance problems plus the loss of heat along the way. The later can be minimized by testing in a vacuum and using radiation shields, but even so, these effects should be quantified in order to know their impact on measurement accuracy.

Certainly, there are some new, "pulse", techniques to measure κ using lasers but this also has its problems. Not the least of which is the fact that measuring κ on one instrument, ρ on another and α on yet another is not very dependable process. This problem is discussed in more detail below.

2.4 Figure of Merit, Z

A method was developed in the early 1960's by T.C. Harman¹ for "directly" testing the Figure of Merit, Z, of a thermoelectric material sample. At very low applied current, where ΔT is very small, the assumption of constant values for α, ρ and κ is very good. As a result, Harman developed the following simple expression relating Z directly to measurable voltages and temperature:

\[ Z = \frac{(V_i - V_r)}{(V_r T_a)} \]  

Where:

\[ T_a = \frac{(T_h + T_c)}{2}: \text{Average temperature of the specimen}. \]

Further discussion is made below on the derivation of this equation and the implied assumptions needed for this simplified expression.

The Harman method provided a direct measurement of Z but lacked precision and reproducibility primarily due to mechanical and electronic limitations of the instrumentation. The biggest problem was in the measurement of \( V_r \), as described above, since it involved the use of an AC method. Originally, Harman used a chopped, DC source to generate a bi-polar, square wave current and used the same
chopper to return the measured square-wave signal to a DC voltage. This was done in order to use the same DC measurement instrument for measuring both voltages. This technique had basically two problems in addition to those described above in section 2.2: (1) It required a "dead-band" at the switch points in order to prevent voltage spikes and (2) The frequency of the voltage source had to be slow enough to avoid inductance problems but significantly faster than the time constant of the specimen.

3. DESIRED TEST SYSTEM CHARACTERISTICS

TE design engineers struggle against both cost and performance in trying to compete against more "conventional" cooling technologies. They cannot afford to add much "safety margin" to their design and still be competitive. Therefore, accurate characterization of TE materials is an essential input to the design process needed to support the continued growth of the TE industry. To that end, TE material and device test technology should encompass the following characteristics:

3.1 Test Z Directly

The single most important TE material parameter is Z. It is the parameter that defines the maximum cooling performance and operating efficiency of TE devices made therefrom. Therefore, the ultimate test system should be able to test Z as directly as possible, rather than rely on the accuracy of the individual parameters, α, ρ and κ. Note that, in the definition of Z, equation (1), the TE specimen geometry totally cancels in the ρκ product. Therefore, if Z could be tested directly, it would be independent of geometrical measurement errors (except for heat loss corrections).

3.2 Simultaneous Measurements

A test method which can simultaneously measure α, ρ and κ will eliminate problems associated with matching up the temperatures of each TE material parameter. That is, even if the individual measurements may have been accurate, if the temperature, or even the temperature distribution, of the α, ρ and κ test are not equivalent, serious errors can be made in the combined Z parameter. Also, changes can occur in specimens due to contamination, contact resistance, etc., during separate test events which will affect Z.

3.3 Thermal Reversibility

The measurement of α, κ, or Z involves significant thermal considerations. As mentioned above, the accuracy of the measurement of α and κ depends upon ΔT. This measurement of this parameter, in turn, can be greatly improved if the specimen can be thermally reversed. Thermal reversal, as used herein, consists of making certain electrical reversals which cause the heat flow through the
specimen to reverse, but make no physical changes in the configuration. If one temperature sensor were to read a little higher than the other, the ΔT will be, say, lower than actual. However, upon thermal reversal, it would be higher than actual. The average of the two, therefore, will correct for this unbalance.

The measurement of κ, or Z involves various thermal heat loading effects. Upon thermal reversal, the measured error is greatly reduced or, in the case of Joule heating in current wires, totally nullified. This will be explained in greater detail below.

3.4 Use The Same Specimen

The use of different specimens for testing α, ρ and κ should be avoided, if possible. This would make the Z measurement accuracy more dependent on geometrical errors. Moreover, this introduces errors due to inexact correlation between samples.

3.5 Use The Same Equipment

The use of different measurement technology, techniques, and/or equipment for testing α, ρ and κ should be avoided, if possible. Such combined-technology for testing a single specimen can produce systematic errors due to imperfect calibration and correlation between test systems.

4. THE TRANSIENT TEST METHOD

A new method has been developed which meets all the specifications given above. It is roughly based on the Harman method but has some fundamental differences which give rise to improvements in accuracy and reproducibility. The fundamental similarity is that both techniques are designed to measure the stable DC voltage, V_i, and resolve its voltage components. The fundamental difference is that the Harman method does this by measuring the resistive component of voltage, V_r; whereas the new method measures the Seebeck component of voltage, V_o. Another fundamental difference is that the new method involves the analysis of transient data.

This new test method presented herein shall be referred to as the "TRANSIENT" test method. The TRANSIENT methodology applies to TE material pellet specimens as well as completed, TE modules consisting of one or more pairs of P and N-type couples.

The key to the TRANSIENT method is a computer driven, high speed, high resolution, integrating voltage measurement system which is capable of accurately resolving the voltage components in an active TE device or sample. The subsequent computer analysis yields measured values for α, ρ, κ, and Z. These parameters are measured simultaneously on the same sample via an absolute method requiring no reference or standard material for comparison.
4.1 General Description

The TRANSIENT method of measuring thermoelectric material parameters was derived by careful examination of the one-dimensional, temperature independent thermoelectric cooling device equation:

$$Q_c = \alpha \Delta T_c - I^2 \rho L / 2A - \kappa \Delta T / L \tag{8}$$

Where:

$$Q_c = \text{Heat supplied to the specimen at the point where } T_c \text{ is measured.}$$

As long as the applied current and $\Delta T$ is small, the assumption of $\alpha$, $\rho$, and $\kappa$ being constant over this range is quite good and this formula, therefore, is sufficiently accurate.

If a suspended sample is powered by the opposing set of current leads, equation (8) will hold and $Q_c$ will be the sum of losses as a result of the environment, leads, etc. The thermal conductivity, $\kappa$, can then be determined from equation (8) by the following equation.

$$\kappa = (V_o T_c / \Delta T - V_r / 2) IL / (A \Delta T) - Q_c L / (A \Delta T) \tag{9}$$

Before specimen installation, $L$ and $A$ are measured. After steady-state is achieved, $I$, $T_h$, $T_c$ and $V_i$ are measured. Via the method described below, $I$ is interrupted, defining $V_o$ and $V_r$. This provides all the factors needed to calculate the first term of equation (9) yielding a quantity which we shall call $\kappa_o$, the "uncorrected" value for $\kappa$. That is, the second term shall be considered as a "correction factor" subtracted from $\kappa_o$ to yield the true value for $\kappa$. Parameters $\alpha$ and $\rho$ are also determined from equations (2) and (4) using the same $V_o$ and $V_r$ values.

This correction factor is determined by accurately modeling the test conditions and configuration taking all possible heat loss factors into consideration. Through mathematical analysis this correction factor can be greatly reduced by using a bi-polar test method. That is, tests are performed sequentially by repeating the test with the DC current reversed. Via this technique, the correction factor for room temperature tests can be reduced to a value of about 8% with the sample in air and about 3% if the test is performed in a vacuum. Certainly, the correction factor can be determined to accuracy values better than 30% yielding an overall accuracy for $\kappa$ of better than 1%!

Of course, this level of precision is dependent upon solving the fundamental problems discussed earlier and obtaining detailed data on the Seebeck probe material. Furthermore, the correction factor percentage will be temperature dependent. It is lower at low temperature and higher at temperatures above room temperature.
Indeed, this measurement technology for high temperature will be increasingly dependent on the accuracy of the thermal loss modeling plus the special methodologies employed for typical high temperature \( k \) testing to minimize ambient effects. Nevertheless, this test technology will still yield the fastest, most accurate results for the TE material parameters. They will also provide maximum closure with device performance data since the test condition itself is a low-level device performance point.

4.2 TE Pellet Test Configurations

Figure 1 illustrates four different test configurations for a TE pellet sample. The first of these is a suspended sample employing a four-probe technique. This test method will be necessary whenever the contact resistance is unknown or significant compared to the resistance of the TE pellet. Copper/constantan thermocouples are attached directly to the TE pellet by resistance welding or some other suitable process. The copper halves of these thermocouples double as voltage probes. Difficulties with the four-probe configuration are that: (1) current flow through the TE pellet can be disturbed by the presence of the thermocouples; (2) voltage pick-up in the probes can result creating significant errors in the thermocouple readings; (3) precise measurements of the probe separation are usually very difficult to obtain; and (4) the voltage and temperature "planes" may be affected by the probes and, therefore, not nearly as well defined at the probes than they are at the opposite ends where high conductivity end caps are applied.

The indicated two-probe configuration is recommended for most TE materials where good contacts are relatively easy to obtain. However, one should be careful to place the current and thermocouples at opposite edges of the end caps in order to avoid voltage pickup in the thermocouples. Essentially, the thermocouple should not be placed in a position on the end cap where current "lines" will intersect it.

The configuration indicated as "HEAT SUNK" is also applicable and, in fact, was used to obtain the temperature dependent data presented in this paper. There was some slight differences in the correction factors and in the measured time constant, but, due to the bi-polar test sequence employed, there was essentially no significant error difference between the suspended and HEAT SUNK configurations. The primary advantageous feature of the HEAT SUNK configuration is that the TE specimen can be thermally attached to the top of a multi-stage TE cooler to easily control its temperature yet maintain a high degree of TE specimen temperature stability.

The "NO THERMOCOUPLES" configuration is usable to obtain \( \rho \) and \( Z \) measurements. Very simple fixtures can be used to obtain "quick" data on these two key material parameters. These tests are very effective for screening samples for potential more rigorous testing. This mode is especially effective for rapid testing TE modules and will be discussed in more detail below.
4.3 TE Module Test Configurations

Examples of some test configurations for a TE module are given in Figure 2. The method used to attach the thermocouples for the SUSPENDED mode was simply to apply a tiny "dab" of thermal compound into which the thermocouple junction was imbedded. It was held in place under compression with scotch tape. This has proven to be very effective technique when properly applied.

Note that, unlike the TE pellet samples, the thermocouples will not be in contact with the active circuit and voltage pickup will not be a factor. However, care must be given to attach voltage probes directly onto the input tabs but not under the same junction as the current probes. This must be done in order to avoid the voltage created by contact resistance, especially if "alligator" clips are used. Dual contact "Kelvin clips" are excellent for this purpose.

As mentioned above, the "NO THERMOCOUPLES" configuration provides the ultimate in simplicity in hook-up and test speed. As will be discussed below, the measured parameters obtainable via this configuration are $\rho$ and $Z$. This is enough to assure the quality of production TE modules. Furthermore, since a +/- 3°C error in absolute temperature, $T_a$, produces only 1% error, the figure of merit, $Z$, is extractable even if the temperature of the TE module is only approximately known, such as in the ambient test of TE modules. For standard production testing of TE modules, a set of algorithms have been derived which predict a "response surface" for $\alpha$ as a function of the measured $\rho$ and $Z$. This data, in turn, is subsequently used to project all of the operating performance parameters of interest.

4.4 TE Assembly Configurations

The TRANSIENT test can be made on a completed assembly as long as the TE power leads can be accessed. Of course, the test time will be increased due to increased thermal masses in contact with the TE module, but this test will still take less time than a full performance test. Furthermore, the TRANSIENT test provides other key system information in addition to a full set of projected system performance curves. That is, comparison with prior TE module test data will yield the overall loss conductance of the system. This will provide a simple, fast and accurate means of evaluating the quality or effectiveness of a given TE assembly with no extra test time. Another important output from the TRANSIENT test is the overall time constant of the system. This information is very useful where system cool-down time is of interest.

4.5 Transient Waveform Analysis

As mentioned above, the basis for the TRANSIENT method is to not measure $V_f$ at all, but measure $V_o$. If one removes the current and instantaneously measure the "residual" voltage, that measured voltage will essentially be $V_o$. The problem is that the time constant for the initial decay of $V_o$, immediately after the current
is removed, is extremely fast. This will be the case even if large thermal masses were attached to the ends of the TE specimen to slow it down. There will be a significant initial decay as a consequence of the time constant of the TE pellet which is usually very small in size and even a few milliseconds will result in significant voltage decay and uncertainty of the true $V_0$. Nevertheless, the TRANSIENT test and analysis technique described herein is capable of precisely determining $V_0$.

The situation is shown graphically in Figures 3 and 4. As current is applied in accordance with Figure 3, the voltage across the TE specimen will be that shown in Figure 4. The voltage rises instantaneously to the value $V_R$ and then asymptotically to a value of $V_0 = V_R + V_0$ at steady-state. As the current is shut off, the voltage drops instantaneously to $V_0$ and decays exponentially to zero. An important aspect of the hardware was to ensure that the current waveform was extremely "clean", i.e. did not contain any "spikes" or anomalies. The method employed was checked with a high speed, high resolution oscilloscope to assure that this condition was indeed met.

The key to the TRANSIENT method was to accurately reconstruct the detail for the waveform of the actual voltage at the precise instant of the switch point. The key to this reconstruction is the utilization of a high speed, high resolution, programmable, integrating, analog-to-digital (A/D) computer board.

An A/D board was obtained which met all of these requirements. It also included a remote terminal board which contained especially designed isothermal terminals for thermocouples together with selfcontained reference junction compensation. It had 16-bit resolution which produced sub-microvolt resolution of the millivolt voltage signals obtained from single TE pellet samples. By way of software selection, a "filter mode" provided for integration of the instantaneous voltage over a specified period of time (approximately 20 milliseconds). This filter mode was one of the keys to this methodology since it yielded the time averaged voltage over this period even for the unusual waveform produced during the "switch point".

The waveform analysis process is illustrated in Figures 5 and 6. Each square represents an actual measured voltage data point of a TE module. These data were obtained via repetitiously measuring the TE module voltage at a known frequency. This measurement shall be referred to herein as the "burst" measurement. At a time of approximately 275 milliseconds from the start of the burst measurement, the applied current to the TE module was abruptly shut off. When this happened, an "intermediate voltage" reading was evident followed by the decaying "residual" voltage. The intermediate voltage reading represented the average voltage made up of the $V_i(t)$ voltage prior to the switch point plus the rapidly decaying $V_0(t)$ voltage after the switch point. This data point was used to determine the exact instant in time of the switch point,
tsw. That is, several test points were curve-fitted with a linear regression process to define the equation of the \( V_1(t) \) curve. Actually, a simple averaging process would have probably sufficed, but the slope from this regression served the dual purpose of double-checking temperature stability. That is, whenever the slope was not very nearly equal to zero, the test was automatically recycled.

A similar process was applied to the first few initial points following the intermediate data point in order to define the equation of the \( V_0(t) \) curve. It is plotted against some of the initial test data points after the switch point as shown in Figure 6. Although the nature of the voltage decay is exponential, it is not a simple exponential since it is made up of several discrete masses connected together. In fact, a simple exponential did not fit very well for the initial set of data points. Further discussion on this subject is given below. In the final analysis, it was discovered that the linear regression of the first three points yielded the most dependable extrapolation of the time dependent \( V_0(t) \) voltage nearby the true switch point time, tsw. Incidentally, notice that a 1.26% error would have resulted from simply accepting the first measured voltage for the value of \( V_0 \). This error could be as much as 6% for small suspended TE pellet samples.

The time, tsw, was calculated by constructing the original waveform using the two curve-fit equations described above and the switch point, tsw, as a variable. An expression was subsequently set up for the area under this zigzagged broken line from the time interval of the last test point before tsw and the "test data point during switch", shown in Figure 5. This expression was set equal to the area over that same time interval using the constant voltage defined by the measured "test data point during switch". With tsw determined therefrom, the true values of \( V_1 = V_1(tsw) \) and \( V_0 = V_0(tsw) \) were defined using the respective extrapolation formulas for \( V_1(t) \) and \( V_0(t) \). Notice that these values are for the same instant in time, tsw. The current, I and temperatures \( T_h \) and \( T_c \) are measured prior to initiating the burst measurement, but many checks and double-checks were made to make sure the TE specimen under test was extremely stable prior to initiating the burst test, as discussed in more detail below.

### 4.6 Temperature Stability

The actual test data of a "extended burst" test was used for determining the time constant of the TE specimen under test. It was calculated from the slope change between data points over the 2 second burst test and was quite well defined and highly reproducible. This was essentially "free" data since the burst test was a basic necessity of the TRANSIENT test technology.

The resulting time constant was not only usable to characterize system cool-down, but was very useful in determining the time needed for temperature stabilization of the specimen under test. That is,
the TE module stabilization time was determined by using 5 to 6 times the time constant.

The significance of this result is that this tested stabilization time is compared with the actual "wait time" prior to initiating the burst sequence. If the wait time had been less, the test was automatically recycled forcing the tested stabilization time on this and all subsequent tests. This process is repeated for each test and the stabilization time is automatically updated as required. The effectiveness of this feature is that it not only allows complete and dependable automation while maintaining test precision but minimizes the wait time and, thus, maximizes overall test speed.

4.7 Thermal Reversal

All TRANSIENT tests are made via a two-step, bi-polar process. That is, the test is performed using one polarity of applied current and then the current is reversed and the test repeated. The primary purpose of this bi-polar process is to create a thermal reversal, as described above. It reduces the magnitude of the correction factors and maximizes the overall accuracy of the results. See Figure 7 for measured correction factors for a typical TE sample in a vacuum.

Bi-polar testing is actually the key to precision testing of all the parameters of the TE specimen. That is, each parameter is calculated from voltage and/or temperature differences. The equations for each parameter derived below reveal this fact. For example, Seebeck coefficient is calculated from two basic quantities: \( V_0 \) and \( \Delta T \). \( V_0 \), in turn, is actually the difference between two voltage measurements and \( \Delta T \) is the difference between two temperature measurements.

Application of the bi-polar method further corrects for any thermal emf's in the test circuit and for imperfections in the thermocouples which might cause them to not be totally identical. Essentially, the accuracy of the results is mostly dependent on the linearity of the measurement system which is an inherently excellent feature of the A/D board used by the TRANSIENT test system.

4.8 Thermal Modeling and Equations

One of the key features of the TRANSIENT test method is the utilization of a very low test current. It is calculated from the input geometry of the TE specimen under test to yield approximately 4°C across the TE specimen. This corresponds to approximately 1/50th of the current that would normally produce maximum \( \Delta T \). This magnitude of \( \Delta T \) provides plenty of signal for accuracy but not so much that it will take the TE specimen below dew point and introduce large condensation heat loads which are difficult to accurately quantify. Also, since the \( \Delta T \) is so small, the assumption of constant parameters is very good making the closed form, simplified heat source equations quite rigorous. These low currents also allow testing of even extremely high current TE material wafers.
The first step in setting up the equations for determining the TE material parameters was to set up expressions for each component of heat flow for the chosen test configuration. These expressions are summarized in Table 1. They include all active and parasitic heat sources applied to a suspended or heat sunk TE module. Very similar expressions can be set up for TE pellet samples and each of the configurations described above.

Table 2 is a set of equations formed from the sum of each corresponding expression taken from Table 1. Note that the wire conduction losses and Joule heat terms are zero as a result of using the same absolute value of applied current in each mode of the bipolar process. Also note that the radiation terms reduce to $T_h^4 - T_c^4$ since the ambient temperature drops out. Since $T_h$ and $T_c$ are set by the experiment to be a small $\Delta T$, the first term in the Taylor expansion is an excellent approximation, as indicated in Table 2. The resultant is that each term below the Peltier term contains the same temperature expression.

The heat balance equation for all non-zero terms from Table 2 is given by:

$$Q_k + Q_{ri} + Q_{re} + Q_c + Q_a + Q_p = 0$$  \hfill (10)

Where:

$Q_p$ = Module Peltier Heat into Junction.
$Q_k$ = Module Conducted Heat into Junction.
$Q_{ri}$ = Internal Radiation Heat into Junction.
$Q_{re}$ = External Radiation Heat into Junction.
$Q_c$ = Convection Heat into Junction.
$Q_a$ = Air Conduction Heat into Junction.

Substitution of the expressions from Table 2 yields an equation for $\alpha/k$ as a function measured parameters multiplied by an overall correction factor, C:

$$\frac{\alpha}{k} = C\Delta T_a / (LX_a)$$  \hfill (11)

Where:

$C = 1 + \text{Radi} + \text{Rade} + \text{Conv} + \text{Cair}.$
$\text{Radi} = 2K_{ri}L/(2Nk)$
$\text{Rade} = K_{re}L/(2Nk)$
$\text{Conv} = HL/(2Nk)$
$\text{Cair} = 2K_aL/(2Nk)$
$\Delta T' = (T_h' - T_c')$
$\Delta T_a = (\Delta T + \Delta T')/2$
$Ta' = (T_h' + T_c')/2$
$X_a = (LI'T_a + LI'T_a')/2$

All other parameters are defined in Table 2.
The overall correction factor, \( C \), is equal to 1 plus a series of dimensionless correction factors derived from each remaining source of parasitic heat load. Each correction factor is a function of \( \kappa \) itself, requiring an iterative calculation process. However, since these factors are typically quite small, convergence is usually achieved in just a few iterations.

Comparison testing in a vacuum versus air has provided a very accurate means of empirically establishing the overall convection and air conduction coefficients used in the corresponding correction terms. This further improved the accuracy of the correction coefficients and of the final test data.

The voltage equations for the TE specimen under test are given by:

\[
\begin{align*}
V_o &= N\alpha \Delta T + \alpha_w \Delta T \\
V_o' &= N\alpha \Delta T' + \alpha_w \Delta T' \\
V_i &= Np\ell I/A + V_o \\
V_i' &= Np\ell I'/A + V_o'
\end{align*}
\] (12) (13) (14) (15)

Note that \( \alpha_w \) is the thermopower of the voltage wires and must be included for all TE pellet calculations. It is included throughout all formulas but simply set to zero for TE modules since both voltage probes will be at the same temperature.

The calculation of \( \alpha \) and \( \rho \) are obtained from the set of voltage equations:

\[
\begin{align*}
\alpha &= V_{oa}/(N\Delta T_a) - \alpha_w \\
\rho &= (V_{ia} - V_{oa})A/(NLI_a)
\end{align*}
\] (16) (17)

Where:

\[
\begin{align*}
V_{oa} &= (V_o + V_o')/2 \\
V_{ia} &= (V_i + V_i')/2 \\
I_a &= (I + I')/2
\end{align*}
\]

The equation for \( \kappa \) was formed by dividing equation (16) by equation (11) to yield the following equation:

\[
\kappa = L X_a V_{oa}/(C N^2 \Delta T_a^2) + L X_a \alpha_w/(C A \Delta T_a)
\] (18)

The equation for \( Z \) was formed by multiplying equation (16) by equations (11) and dividing by equation (17) to yield the following equation:

\[
Z = CV_{oa}I_a/X_a/(V_{ia} - V_{oa}) - CI_a\alpha_w/N/\Delta T_a/X_a/(V_{ia} - V_{oa})
\] (19)
Note that each term on the right side of equations 16, 18 and 19 are measurable parameters yielding a truly absolute test methodology for each TE material parameter. Also note that the second terms of these equations go to zero for a TE module or when $\alpha w$ can be ignored compared to $\alpha$. If this is applied together with the realization that $I_a/X_a$ is nearly equal to $1/T$ (for perfect reversal), Equation 17 reduces to the well-known Harman formula:

$$ZT = \frac{V_{oa}}{(V_{ia}-V_{oa})} \quad \text{(for } C = 1)$$

(20)

This simplified formula accounts for the fact that the resultant $Z$ test data (presented below) exhibits very low scatter, since it is primarily dependent on $V_o$ and $V_i$ which are accurately measurable via the TRANSIENT test method.

4.9 Experimental Data

To illustrate the output obtainable from the TRANSIENT test system, Temperature dependent TRANSIENT testing was performed on one "standard" and one "special" TE pellet sample. Both samples were $2\text{mm square} \times 1.65\text{mm long}$ TE pellets installed in the "HEAT SUNK" configuration on top of a multi-stage TE cooler in a vacuum.

The test data collected on both samples (tested 3 times each) are given in Figures 8-11. The correction factors for these tests are given in Figure 7. The following observations were made: (1) The resistivity scatter was very low since the data was not dependent on thermocouples, correction factors or vacuum level. (2) The Seebeck scatter was not quite as good because of the dependence on $\Delta T$ measurements. Nevertheless, the scatter was still quite low because of the special care given to precision thermometry. (3) The thermal conductivity scatter was largest as expected since these measurements were affected by correction factors, thermocouples and vacuum level. (4) The $Z$ scatter was better than the thermal conductivity scatter because it was not affected by thermocouples as explained above. (5) Overall, the reproducibility was excellent to the point that it is difficult to identify the three separate measurements made for each parameter at each temperature point.

Finally, the importance of the precision and flexibility of the TRANSIENT test methodology presented herein is exemplified in Figure 11. The $Z$ versus temperature for the standard sample is quite typical for "normal Bismuth-Telluride" TE materials. If only tested at room temperature, the "special" TE material produced at TE Technology, Inc. would not have identified any significant $Z$ enhancement. However, its low temperature $Z$ data represents unusually high performance. It would greatly improve the cooling performance of a low temperature multi-stage cascade.
5. DISCUSSION AND SUMMARY

A new TRANSIENT test methodology has been developed and has been described in detail. It provides the basis for a high speed, high precision measurement system for thermoelectric ingots, wafers, pellets, modules and systems. It offers significant improvements but maintains all of advantageous features of the Harman\textsuperscript{1} method.

The TRANSIENT technique employs a detailed thermal model created for the TE specimen under test automatically by the computer software. The software drives a PC computer with a special A/D board plugged into an expansion slot of the computer. The test sequence employs a transient technique and extracts the key TE material parameters via analysis of the digital waveform data. Rigorous formulas are used which separate the "zero order" TE material ZT and thermal conductivity terms from several correction terms involving internal radiation, external radiation, air conduction, external convection and, in the case of single TE pellets, conduction through the test wires and thermocouples.

Data have been presented on TE modules and samples which validate the claims for this test methodology. It is simple, fast accurate and very easy and affordable to use. It is, therefore, presented to the thermoelectric community for consideration as the standard for the industry. Since it is particularly accurate in its measurement of ZT, this test technology will virtually eliminate conflicts in TE quality claims that might otherwise arise between the various TE organizations of the world.

REFERENCE:
Figure 1: Test configurations for a TE pellet sample.

Figure 2: Test configurations for a TE module.

Figure 3: Current pulse applied to a TE specimen.

Figure 4: Transient voltage due to the Figure 3 current pulse.
Figure 5: Determination of switch time, $t_{sw}$, and corresponding voltages $V_i(t_{sw})$ and $V_o(t_{sw})$.

Figure 6: Analysis of data immediately following the switch point.

Figure 7: Correction factors for a 2mm square x 1.6mm long TE pellet sample mounted onto the top stage of a multi-stage thermoelectric cooler in a vacuum of 10 milliTorr.
Figure 8: Electrical resistivity test data taken on standard and special N-type TE pellets.

Figure 9: Seebeck coefficient test data taken on standard and special N-type TE pellets.

Figure 10: Thermal Conductivity test data taken on standard and special N-type TE pellets.

Figure 11: Figure of merit test data taken on standard and special N-type TE pellets.
<table>
<thead>
<tr>
<th>HEAT LOAD DESCRIPTION</th>
<th>HEAT ENTERING COLD JUNCTION</th>
<th>HEAT EXITING HOT JUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Module Peltier</td>
<td>$-NaIT_c$</td>
<td>$-NaIT_h$</td>
</tr>
<tr>
<td>2. Module Conduction</td>
<td>$NkA(T_h - T_c)/L$</td>
<td>$NkA(T_h - T_c)/L$</td>
</tr>
<tr>
<td>3. Internal Radiation</td>
<td>$R_i(T_h^4 - T_c^4)$</td>
<td>$R_i(T_h^4 - T_c^4)$</td>
</tr>
<tr>
<td>4. External Radiation</td>
<td>$R_e(T_x^4 - T_c^4)$</td>
<td>$R_e(T_h^4 - T_x^4)$</td>
</tr>
<tr>
<td>5. Convection</td>
<td>$H(T_x - T_c)$</td>
<td>$H(T_h - T_x)$</td>
</tr>
<tr>
<td>6. Air Conduction</td>
<td>$K_a(T_h - T_c)$</td>
<td>$K_a(T_h - T_c)$</td>
</tr>
<tr>
<td>7. Wire Conduction</td>
<td>0</td>
<td>$W(T_h - T_w)$</td>
</tr>
<tr>
<td>8. Module Joule</td>
<td>$I^2R/2$</td>
<td>$-I^2R/2$</td>
</tr>
<tr>
<td>9. Wire Joule</td>
<td>0</td>
<td>$-I^2R_w$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HEAT LOAD DESCRIPTION</th>
<th>HEAT ENTERING COLD JUNCTION</th>
<th>HEAT EXITING HOT JUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Module Peltier</td>
<td>$-NaI'T_c'$</td>
<td>$-NaI'T_h'$</td>
</tr>
<tr>
<td>2. Module Conduction</td>
<td>$NkA(T_h' - T_c')/L$</td>
<td>$NkA(T_h' - T_c')/L$</td>
</tr>
<tr>
<td>3. Internal Radiation</td>
<td>$R_i(T_h'^4 - T_c'^4)$</td>
<td>$R_i(T_h'^4 - T_c'^4)$</td>
</tr>
<tr>
<td>4. External Radiation</td>
<td>$R_e(T_x'^4 - T_c'^4)$</td>
<td>$R_e(T_h'^4 - T_x'^4)$</td>
</tr>
<tr>
<td>5. Convection</td>
<td>$H(T_x' - T_c')$</td>
<td>$H(T_h' - T_x')$</td>
</tr>
<tr>
<td>6. Air Conduction</td>
<td>$K_a(T_h' - T_c')$</td>
<td>$K_a^*(T_h' - T_c')$</td>
</tr>
<tr>
<td>7. Wire Conduction</td>
<td>$W(T_w - T_c')$</td>
<td>0</td>
</tr>
<tr>
<td>8. Module Joule</td>
<td>$I'^2R/2$</td>
<td>$-I'^2R/2$</td>
</tr>
<tr>
<td>9. Wire Joule</td>
<td>$I'^2R_w$</td>
<td>0</td>
</tr>
</tbody>
</table>
**TABLE 2**

SUM OF JUNCTION HEAT LOAD CALCULATIONS FOR A TE MODULE

1. Module Peltier: \( Q_p = -N\alpha(I(T_h + T_c) + I'(T_h' + T_c')) \)

2. Module Conduction: \( Q_k = 2N\kappa A(T_h - T_c + T_h' - T_c')/L \)

3. Internal Radiation: \( Q_{ri} = 2K_{ri}(T_h - T_c + T_h' - T_c') \)

4. External Radiation: \( Q_{re} = K_{re}^*(T_h - T_c + T_h' - T_c') \)

5. Convection: \( Q_c = H(T_h - T_c + T_h' - T_c') \)

6. Air Conduction: \( Q_a = 2K_a(T_h - T_c + T_h' - T_c') \)

7. Wire Conduction: \( Q_w = 0; \text{Since } T_w = T_h = T_c' \)

8. Module Joule: \( Q_{mj} = 0; \text{Since } I = I' \)

9. Wire Joule: \( Q_{wj} = 0; \text{Since } I = I' \)

Where:

- \( N = \text{total number of TE pellets} \)
- \( \alpha = \text{TE material Seebeck coefficient} \)
- \( I, I' = \text{Electrical current in POS \& NEG modes} \)
- \( T_h, T_h' = \text{Hot junction temperatures in POS \& NEG modes} \)
- \( T_c, T_c' = \text{Cold junction temperatures in POS \& NEG modes} \)
- \( T_x = \text{Ambient temperature} \)
- \( \kappa = \text{TE material Thermal conductivity} \)
- \( L = \text{Length of TE pellet} \)
- \( A = \text{Area of TE pellet} \)
- \( R_i = \sigma \varepsilon * \text{Internal surface area} \)
- \( R_e = \sigma \varepsilon * \text{External surface area} \)
- \( \sigma = \text{Boltzman constant} \)
- \( \varepsilon = \text{Effective emissivity (including shape factor)} \)
- \( H = \text{Convection coefficient * External surface area} \)
- \( K_a = \text{Air conductivity * Internal space area} \)
- \( W = \text{Sum of wire thermal conductances} \)
- \( R = \text{TE Module electrical resistance} \)
- \( R_w = \text{Electrical current wire electrical resistance} \)
- \( T = \frac{(T_h + T_c)}{2} \)
- \( T_h^4 - T_c^4 = 4T^3a(T_h - T_c), \text{(Taylor approximation)}. \)
- \( K_{ri} = 4T^3R_i \)
- \( K_{re} = 4T^3R_e \)