Device Testing and Characterization of Thermoelectric Nanocomposites

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Abstract

It has become evident in recent years that developing clean, sustainable energy technologies will be one of the world’s greatest challenges in the 21st century. Thermoelectric materials can potentially make a contribution by increasing energy efficiency of some systems. Thermoelectric materials may play a role in the large scale energy industry, specifically in the applications of refrigeration and waste heat recovery.

In this work a novel thermoelectric material will be tested for conversion efficiency. A Bi$_2$Te$_3$ nanocomposite has been developed by the joint effort of Prof. Gang Chen’s group at MIT and Prof. Zhifeng Ren’s group at Boston College. The material exhibits enhanced thermoelectric properties from optimized nanoscale structures and can be easily manufactured in large quantities. In order to better characterize its performance a novel power conversion measurement system has been developed that can measure the conversion efficiency directly. The measurement system design will be described in detail; important design considerations will be addressed such as measuring heat flux, optimizing the load matching condition and reducing electrical contact resistance. Finally the measured efficiency will be compared to the calculated efficiency from a temperature-dependent properties model.

It will be shown that a Ni layer must be attached to the nanocomposite to allow soldering and power conversion testing. Results of this work will show that the nanocomposite efficiency is higher than the commercial standard. Electrical contact remains a challenge in realizing the potential efficiency.

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Chapter 1: Introduction

The field of thermoelectricity examines the direct coupling of electricity and heat within a material. Thermoelectric (TE) devices operate as heat engines or heat pumps and are appealing because they have no moving parts, are highly reliable, and are easily scaled in size[1]. However, their efficiency needs to be improved if they are to be broadly implemented beyond a few niche markets, and be competitive with current energy conversion technology on a large scale [1]. It’s been evident in recent years that nanostructured thermoelectrics offer the greatest potential for increasing conversion efficiency [2]. Thermoelectric properties are dominated by the transport characteristics of electrons and phonons which have mean free paths on the order of nanometers. Nanostructures close to this length scale or smaller can strongly affect electron and phonon transport and enhance thermoelectric properties if designed properly [3]. This chapter introduces the Seebeck effect and Peltier effect, the fundamental equations of thermoelectricity and provides an overview of the state-of-the-art in the field.

1.1 Thermoelectric Phenomena

When a material is subjected to a temperature difference, an electrical potential difference is produced (Fig. 1.1a), conversely, when electrical current flows through a material, heat energy is also moved. These phenomena are called thermoelectric effects, the former is called the Seebeck effect and the latter is called the Peltier effect, named after the scientists who first observed these phenomena [4]. Fig. 1.1 shows the thermoelectric effects in a single material. The fundamental physical reason for
thermoelectric phenomena is that charge carriers such as electrons and holes, are also heat carriers. Heat transfer and current flow are thus coupled phenomena, and will be briefly explained in the following two sections.

![Diagram of thermoelectric effects](image)

**Figure 1.1** Thermoelectric effects in a material. a) Seebeck effect: a temperature difference induces a voltage through the material b) Peltier effect: a current flow induces heat flow through the material

### 1.1.1 Seebeck Coefficient

The Seebeck effect has been used in thermocouples to measure temperature, for a long time. Conventional thermocouples are made of metals or metal alloys. They generate small voltages that are proportional to an imposed temperature difference. This is the same Seebeck effect which is used in thermoelectric power conversion.

When the electrical current in a material is zero and a temperature gradient is present, an electric potential $\Delta V$ proportional to the temperature difference will develop. The proportionality constant between the temperature gradient and the generated electric potential is called the Seebeck coefficient, defined below.

$$\alpha \equiv -\frac{dV}{dT} \quad (1.1.1)$$

In principle the thermoelectric effect is present in every material but semiconductor materials are currently the best thermoelectrics (see section 1.4).
following offers a simplified explanation of the mechanism that gives rise to the Seebeck coefficient in semiconductors.

Let us consider a non-degenerately doped semiconductor. As the temperature increases in the material so does the chemical potential, and thus the equilibrium carrier concentration. Therefore when a temperature gradient is imposed in a material, a carrier concentration gradient will also be present. More charge carriers are generated on the hot side and diffuse to the cold side creating an internal electric field that resists further carrier diffusion (Fig 1.2). The steady state electrochemical potential difference between the two ends at different temperature is the Seebeck voltage.

![Figure 1.2: The Seebeck effect is when an electric field arises due to the diffusion of charge carriers.](image)

### 1.1.2 Thermodynamics and Peltier Heat

This section will show that thermodynamically there is expected to be a direct coupling between heat transfer and electric current by the Seebeck coefficient. A constitutive relation for heat transfer will be derived to include the Peltier heat. The current density $J$, and heat flux $q$, are inherently coupled phenomena and are linearly proportional to two intrinsic property gradients: the electrochemical potential and temperature [5].

$$
\bar{J} = L_{11}(-\nabla V) + L_{12}(-\nabla T)
$$  \hspace{1cm} (1.1.2)
\[
\tilde{q} = L_{21} (-\nabla V) + L_{22} (-\nabla T) \tag{1.1.3}
\]

The coefficients are calculated based on transport theories, such as the Boltzmann equation. The cross term coefficients \(L_{12}\) and \(L_{21}\) are related by Onsager’s reciprocity theorem: \(\frac{L_{21}}{L_{12}} = T\) [6]. Observe that when the temperature is uniform Eq.1.1.2 becomes the familiar Ohm’s law and \(L_{II}\) is equal to the electrical conductivity \(\sigma\). By setting the current density to zero it is found that the Seebeck coefficient is equal to the ratio of \(L_{12}\) to \(L_{II}\).

\[
\alpha = \frac{L_{12}}{L_{II}} \tag{1.1.4}
\]

We can now rearrange the charge transport equation to get a useful equation for the voltage in which the first term is generated by an Ohmic voltage drop and the second term is generated by the Seebeck effect.

\[
dV = -\frac{J}{\sigma} dx - \alpha dT \tag{1.1.5}
\]

Eliminating \(\nabla V\) from Eq. 1.1.2 and 1.1.3 we arrive at the constitutive relation for heat flux in its final form

\[
\tilde{q} = \frac{L_{21}}{L_{12}} \alpha \tilde{J} - \left( L_{22} - \frac{L_{21} L_{12}}{L_{11}} \right) \nabla T = \Pi \tilde{J} - k \nabla T \tag{1.1.6}
\]
where $\Pi \equiv T\alpha = \frac{L_1\alpha}{L_2}$ is the Peltier coefficient and $k$ is the thermal conductivity. The first term in Eq.1.1.6 is the Peltier heat (below) which is reversible with the direction of the current. This is what allows for thermoelectric heat pumping because the heat is transferred in the direction of the current, independent of the temperature gradient.

$$q_{\text{Peltier}} = \Pi \bar{J}$$  \hspace{1cm} (1.1.7)

Heat is absorbed or released at the interface of two dissimilar materials by the Peltier Effect, Fig. 1.3. When current is conducted across two similar materials, a heat transfer will take place at the boundary due to the different Peltier coefficients of each material. The Peltier heat term allows for thermoelectric refrigeration because heat can be transferred in a direction opposite the temperature gradient by simply controlling the current direction.

Figure 1.3: Peltier heat flow in a segmented material at uniform temperature. Heat transfer is localized at the interface where the Seebeck coefficient changes.
It is generally understood that heat flux is associated with entropy flux via \( \dot{q} = T \dot{J}_s \). Dividing Eq. 1.1.6 by absolute temperature leads to

\[
\dot{J}_s = \alpha \dot{J} - \frac{k}{T} \nabla T
\]  

(1.1.8)

The above equation reconfirms that the Seebeck coefficient is actually the entropy carried per particle.

Physically, charge carriers carry entropy proportional to the Seebeck coefficient. The Seebeck coefficient is like a specific heat that when multiplied by temperature determines the internal energy of the charge carrier. When an electron crosses an interface it enters a different material system with different available electron energy states. The entropy of the electron changes with the Seebeck coefficient and the electron undergoes a heat transfer with the lattice. In principle this is an isothermal heat transfer which occurs near the interface and is reversible with no entropy generation. Advanced transport theory from the Boltzmann equation reveals that the actual interface region has a thickness on the order of the mean free path of an electron and the temperature of the lattice may not be uniform.

### 1.2 Governing Equation of Thermoelectricity

This section will derive the governing equation for thermoelectricity by using the constitutive relation for heat flux from the last section. Later this equation will be used to solve for the heat and work transfers on the boundaries of a thermoelectric device. Let’s consider an energy balance over an element of a thermoelectric material, Fig. 1.4.
Energy is transferred in and out of the boundaries by three mechanisms: Peltier heat, Fourier heat conduction, and electrochemical potential.

Figure 1.4: Energy balance in a differential element of a thermoelectric material. From left to right: Peltier heat, Fourier heat conduction, electrical power.

An energy balance is applied to the volume element and 1st order Taylor series expansions performed on each term to give the following equation.

\[-J \frac{d\alpha T}{dx} + \frac{d}{dx}\left( k \frac{dT}{dx}\right) - J \frac{dV}{dx} = 0 \quad (1.2.1)\]

The change in voltage can be rewritten from Eq.1.1.5 to yield the following.

\[\frac{\partial}{\partial T}\left( k \frac{dT}{dx}\right) \frac{dT}{dx} - JT \frac{\partial \alpha}{\partial T} \frac{dT}{dx} + J^2 \rho = 0 \quad (1.2.2)\]

The above equation is a 2nd order, non linear, PDE, and there are two methods to solving it. One method is to make use of a similarity variable to transform it into a 1st order, non linear ODE; this will be done in chapter 3. The second method which will be applied here is to make a simplistic assumption that all the properties are independent of
temperature. This assumption is only valid over small temperature differences; chapter 3 will discuss the case when this assumption is not valid. Holding $\alpha, k, \rho$ constant we can rewrite Eq.1.2.2 as the following [4].

$$k \frac{d^2T}{dx^2} + J^2 \rho = 0$$

(1.2.3)

The above equation can be solved with 2 boundary conditions $T|_{x=L} = T_c$ and $T|_{x=0} = T_H$ to solve for the temperature everywhere. The hot and cold side heat transfers $Q_H$ and $Q_C$ have contributions from the Peltier heat and Fourier heat conduction, Figure 1.4. The Fourier heat is found by solving for the temperature gradient at the boundaries from Eq.1.2.3. The hot and cold side heat transfers are solved for below

$$Q_H = I \alpha T_H + \frac{kA\Delta T}{L} - \frac{I^2 R_i}{2}$$

(1.2.4)

$$Q_C = I \alpha T_c + \frac{kA\Delta T}{L} + \frac{I^2 R_i}{2}$$

(1.2.5)

where $L$ is the total length of the material and $R_i$ is the electrical resistance. The generated electrical power is solved by subtracting $Q_H$ from $Q_C$

$$P_E = I \alpha \Delta T - I^2 R_i$$

(1.2.6)

The equations for heat transfer have contributions from three terms: the first term is the Peltier heat, the second term is the Fourier conduction heat, and the third term is from a dissipative Joule heating process. Ideally, the Peltier heat term would dominate in a good thermoelectric because the other terms are viewed as losses. The Fourier conduction terms represents heat that is conducted by the temperature gradient in the lattice rather than carried in the current. The Joule heating term is from
electrical work dissipating in the element which leads to unwanted heating in heat pump mode, or electrical power loss in power conversion mode.

Thermoelectric power generation and refrigeration manifests by the thermodynamically reversible Peltier heat transfers at the two interfaces. The bulk of the material is needed only as a conduit for charge carriers to travel between the two interfaces at high and low temperature. The other two properties $k$ and $\rho$, represent intrinsic losses in the conduit. The thermal conductivity represents an additional path for heat to flow parallel to the heat carried by the electric current. The electrical resistivity represents power dissipated by carrier transport.

### 1.3 Power Conversion and ZT

Now that the governing equation for thermoelectricity is built it can be applied to a real device to solve for the energy conversion efficiency. A new property called the figure of merit $Z$, will be defined which fully characterizes energy conversion efficiency. Consider a constant property, Thermoelectric (TE) material operating as a heat engine with ends maintained at constant temperature and connected to an external load. The TE element is referred to as a TE leg the current and heat transport is assumed to be one dimensional and energy is conserved along the length (no heat loss at surface). The ends are connected to an electrical resistor by perfect conductors with a Seebeck coefficient equal to zero, so that thermoelectric effects in the leads are neglected. Each boundary has three energy terms: the Peltier heat, Fourier conduction heat and a Joule heating term. The electrical power term is now replaced by the load resistance, Fig.1.5.
The conversion efficiency is equal to the electrical power dissipated in the load resistance over the hot side power input.

$$\eta = \frac{P_{\text{electrical}}}{Q_H} = \frac{I^2 R_L}{I \alpha T + \frac{kA \Delta T}{L} - \frac{I^2 R_i}{2}}$$ (1.3.1)

Let us substitute in the resistance ratio $M = R_L / R_i$, where $R_i$ is the internal resistance of the TE leg and $R_L$ is the load resistance of the external circuit. The current is rewritten as

$$I = \frac{\alpha \Delta T}{R_i (1 + M)}.$$  The efficiency is now rewritten in terms of the Carnot efficiency times the second law efficiency.
\[ \eta = \eta_c \eta_H = \eta_c \frac{1}{\left(1 + M\right)^2 + \left(1 + \frac{T_c}{T_H}\right) \frac{Z T M}{2M} + 1} \]  

(1.3.2)

where \( \eta_c = 1 - \frac{T_c}{T_H} \) is the Carnot efficiency and \( Z = \frac{\alpha^2}{\rho k} \) is a combination of material properties called the figure of merit. Eq. 1.3.2 is a general equation for efficiency given the boundary temperatures, the thermoelectric material properties and resistance ratio, \( M \).

However to find the maximum efficiency we must use the relation \( \frac{d\eta}{dM} = 0 \) to find the load matching condition corresponding to a maximum efficiency. Upon differentiating Eq.1.3.2 with respect to \( M \) an optimal load matching condition and maximum efficiency are found below

\[ M = \sqrt{1 + \bar{ZT}} \]  

(1.3.3)

\[ \eta = \eta_c - \frac{1}{M + \frac{T_{cold}}{T_{hot}}} = \eta_c \frac{1}{\sqrt{1 + \bar{ZT}}} - 1 \]  

(1.3.4)

where \( \bar{T} \) is the mean temperature and \( \bar{ZT} = \frac{\alpha^2 \bar{T}}{\rho k} \) is called the dimensionless figure of merit. \( ZT \) is the most useful non-dimensional number the thermoelectric community employs because this property alone determines the heat to electrical work conversion efficiency. The commercial standard TE has \( \bar{ZT} \leq 1 \). A common assumption in device design is to assume \( \bar{ZT} \) is constant over a limited temperature range. This assumption
will be looked at more closely in chapter 3. A similar treatment can be done for a TE heat pump and will yield similar results for the importance of the figure of merit [2].

**1.4 Semiconductors as Thermoelectrics**

Good TE materials have a high figure of merit and therefore require a high Seebeck coefficient, a high electrical conductivity, and a low thermal conductivity. This is a very unusual combination of properties; for instance, usually good electrical conductors like metals also have high thermal conductivity. While most thermally insulating materials like plastics and ceramics are also electrically insulating. This section will explain why semiconductor materials hold the greatest potential as TEs. The three thermoelectric properties $\alpha, k, \rho$ are not independent, so it is hard to change only one property without changing the others. For example, increasing the number of electrical carriers not only increases electrical conductivity but also increases thermal conductivity, and decreases Seebeck coefficient. Both electrons and phonons (lattice vibrations) contribute to the thermal conductivity of a material; the electron contribution dominates in metals. The Seebeck coefficient is inversely proportional to carrier concentration [7]. Fig. 1.6 illustrates each of three properties as a function of carrier concentration. As the figure shows, metals have high electrical conductivities, but also high thermal conductivities and low Seebeck coefficients. Insulators have high Seebeck coefficients and potentially low thermal conductivities, but these properties are countered by low electrical conductivities. The best thermoelectric materials which produce the highest $ZTs$ are semiconductors. Moreover, in semiconductors electrical conductivities
and carrier type can be easily changed with minimal affect to other properties, simply by changing the doping type and doping concentration. With dopants, electrical conductivity of semiconductors can reach up to the order of $10^5$ S/m. The contribution of electrons to thermal conductivity is not dominant for semiconductors, so a change in doping concentration has a minor effect on thermal conductivity. Optimizing the doping concentration is an important aspect of developing thermoelectric materials.

Figure 1.6: Thermoelectric properties $S$, $\sigma$, $k$ (Seebeck coefficient, electrical conductivity, thermal conductivity) as a function of carrier concentration. Semiconductors make the best thermoelectric materials.

1.5 State of the Art and Device Design

Thermoelectric devices operate as heat engines or heat pumps and are primarily made from semiconductor materials. When the majority of electrical carriers are electrons, i.e., an n-type semiconductor, the Seebeck coefficient and the Peltier coefficient have
negative values because direction of electron movement is opposite to that of the current. On the other hand, when the majority of electrical carriers are holes, i.e., a p-type semiconductor, the Seebeck coefficient and the Peltier coefficient have positive values. Thermoelectric devices are made with pairs of p-type and n-type TE elements or “legs”. A p-type leg is arranged electrically in series and thermally in parallel with an n-type leg to form a “thermocouple couple”. Figure 1.7 shows a schematic of a typical thermocouple running as a heat engine and as a heat pump.

Figure 1.7 Schematic of thermoelectric devices: power generator (left) and thermoelectric cooler (right)

TE devices have been used in a several niche markets like small scale refrigeration, and radioisotope generators. The most successful long term implementation of TE devices has been in NASA's deep-space spacecraft where thermoelectrics have been used to generate power from a radioisotope (nuclear) fuel source, Fig. 1.8b. When a spacecraft travels to the outer solar system, solar radiation is too weak to be used as an energy source. In this case, the spacecraft’s electrical power is generated by a thermoelectric heat engine operating between a hot nuclear fuel source and cold space. One such RTG weighs about 55 kg and produces about 240 Watts of electricity at about 7% conversion efficiency. The hot side is maintained at 1300 K by a
graphite-encased plutonium heat source and the cold side radiates heat into space at 600 K. There is no ‘off’ switch: the radioisotope has a half-life of 87 years[8]. TE refrigerators have recently been used in high-end automobile seats to deliver temperature controlled air throughout the seats, Fig. 1.8a.

Thermoelectric devices have several advantages in their design and operation:

1) No moving parts. Thermoelectrics are solid state materials with no moving parts, no acoustic noise, and the material itself requires no maintenance. The entire system design is greatly simplified over conventional cycles because there is no working fluid and fewer components.

2) Reliability. TE materials are very stable when operated in the proper temperature range. NASA has used TE generators in missions lasting for decades and even in the harsh environment of space these generators have accumulated more than a trillion device-hours without a single failure [8].

Figure 1.8: TE devices a) TE cooler in a car seat b) TE generator used in NASA space missions
3) Scalability. TE devices can be implemented in anything from integrated circuits and MEMs to industrial sized waste heat recovery and can have high power densities. TE devices are easily scalable over a huge range but are outcompeted by other heat engine and refrigeration cycles at large scale.

4) Reversible. TE devices can be switched from power generation mode to refrigeration mode simply by reversing the current, allowing for superior temperature control.

Fig. 1.9 plots the second law efficiency from Eq.1.3.4 versus ZT. It is believed that TEs could begin replacing large scale refrigeration cycles at ZTs around 3-4 corresponding to second law efficiencies of 38-45%[2]. Thermoelectric generator (TEG) second law efficiencies may never be directly competitive with traditional large scale heat engines like steam and gas turbines that have second law efficiencies above 60%. However TEGs may play a large role in combined cycle applications where TEGs operate at the hot side of an existing heat engine such as in a steam boiler or the cold side—known as waste heat recovery—such has in the exhaust stream of an IC engine.
Over the last several decades the non-dimensional figure of merit has remained at a maximum value of about unity. However, recent developments in nanostructured thermoelectric materials have produced significantly higher figures of merit, Fig. 1.10. Research at NASA-JPL, MIT-Lincoln Labs, Michigan State University, and other organizations from about 1995 to the present has led to the discovery, characterization, and laboratory-demonstration of a new generation of TE materials: skutterudites, thin-film superlattice materials, quantum well materials, and PbAgSbTe (LAST) compounds and their derivatives[1]. These materials have either demonstrated $ZT$ of $\sim 1.5-2$ or shown great promise for higher $ZT$ approaching 3 or 4. Quantum well materials include 0-dimensional (0-D) dots, 1-dimensional (1-D) wires and 2-D thin-film materials.
These materials make it possible to create TE systems that display higher $ZT$ values than those obtained in bulk materials because quantum well effects tend to accomplish two important effects: 1) they tend to significantly increase density of states which increases the Seebeck coefficient in these materials; and 2) they tend to de-couple the electrical and thermal conductivity allowing quantum well materials to exhibit low thermal conductivities without a corresponding decrease in electrical conductivity. The LAST compounds have shown embedded nanostructures within the crystal matrix that may exhibit quantum well effects[1].

Figure 1.10: Timeline of $ZT$ over the past 60 years

TE materials have temperature dependant properties and temperature dependant $ZT$ values. Each material has a finite operating temperature range around the maximum $ZT$ value which means if a device is to operate over a large temperature range then more than one material system must be employed. Fig. 1.11 plots the temperature dependant $ZT$ values for different material systems.
Figure 1.11: ZT vs. temperature for different material systems. Bi$_2$Te$_3$ is the most common room temperature TE.

Although there are many reports of nano-featured TE materials with high ZT's, few of these materials can be fabricated economically or in sufficient quantities. Bi$_2$Te$_3$ is the best bulk thermoelectric around room temperature and is the only commercially available TE. Bi$_2$Te$_3$ has been widely used in small scale refrigeration for decades and has recently been seriously considered for power generation. Researchers have taken a renewed interest in thermoelectric power generation in light of pressing issues of energy and environment the world faces in the 21st century. The challenge is to create a TE material that is economical and scalable to large systems in order to improve energy efficiency and energy conservation.

In the next chapter a high ZT nanocomposite will be introduced. The purpose of the following work is to develop a power conversion measurement system in order to test and characterize the nanocomposite performance. The measurement system will be
designed to measure conversion efficiency under the same conditions of a real thermoelectric generator. A temperature dependant model will be used to compare the predicted performance with experimental results
Chapter 2: Bi$_2$Te$_3$ Nanocomposite

The Bi$_2$Te$_3$ material system is the only commercially available TE material and one of the most well studied. The $ZT$ for this alloy is around 1 at room temperature which makes it very attractive for refrigeration and waste heat recovery applications. Bi$_2$Te$_3$ was thus the logical choice of material systems to implement a novel nanocomposite approach on. This chapter will describe the synthesis and individual property measurements of the Bi$_2$Te$_3$ P-type nanocomposite. This work represents a collaborative effort between Dr. Chen’s group at MIT and Dr. Ren’s group at BC. The results where recently published in [9].

2.1 P-type Bi$_2$Te$_3$ nanocomposite

The dimensionless thermoelectric figure-of-merit ($ZT$) in bulk bismuth antimony telluride alloys has remained around 1 for more than 50 years. We’ve shown that a peak $ZT$ of 1.4 at 100°C can be achieved in p-type nanocrystalline bismuth antimony telluride bulk alloy. These nanocrystalline bulk materials were made by hot pressing nanopowders ball-milled from crystalline ingots under inert conditions. Thermoelectric property measurements and microstructure studies that the $ZT$ improvement is the result of low thermal conductivity caused by increased phonon scattering by grain boundaries and defects. This nanocomposite approach may allow the development of high performance bulk thermoelectric materials at low cost.

In the past researchers have successfully increased $ZT$ in superlattices due to a reduced thermal conductivity [10,11]. The nanocomposite approach uses the same strategy of introducing nanoscale, lower dimensional structures but in a three dimensional
randomly oriented way. The nanoscale grains effectively increase phonon scattering without adversely affecting the Seebeck coefficient and electrical conductivity. As opposed to thin films the P-type Bi$_2$Te$_3$ nanocomposite bulk properties are nearly isotropic. Other thin film methods grow the material layer by layer, which is a very slow and expensive process. The nanocomposite method is based on ball milling and hot-pressing of nanoparticles into bulk ingots. This approach is simple, cost effective, and can be applied to other materials.

It is known that hot pressed TE material can be readily made into segmented legs where more than one TE material is stacked in series [12]. In this way the nanocomposite can be easily used in high temperature power generation applications where segmented legs are employed. Nanocomposites do not suffer from the cleavage problem that is common in traditional zone-melting made ingots, which leads to easier device fabrication and system integration, and a potentially longer device lifetime [9].

2.2 Sample Preparation

All nanocomposite samples were fabricated at Boston College (BC). Nanopowders were prepared by ball milling bulk p-type BiSbTe alloy ingots [13]. Bulk disk samples of 1¼ to 2½ cm in diameter and 2 to 15 mm thick were made by hot-pressing the nanopowders loaded in 1¼ to 2½ cm (inner diameter) graphite dies[13]. Disks of 1¼ cm (diameter) and 2 mm thick, and bars of about 2 mm by 2 mm by 12 mm, were cut from both the axial and disk plane directions. The disks and bars were also polished for electrical and thermal conductivity and for Seebeck coefficient measurements.
To achieve high ZT, control of the size and quality of the starting nanoparticles is essential. TEM images of the ball-milled powder show that the particle size is between 5 and 50 nm with a mean of about 20 nm (Fig. 2.1 C and D). Detailed microstructure studies by BC show that in general, most of the grains are nanosized (Fig. 2.1 A and B). Furthermore, these nanograins are highly crystalline, completely random (large angles between adjacent lattice planes) and have very clean boundaries between grains.

Figure 2.1: A and B) TEM images of nanograins after hot pressing C) TEM image after ball milling D) TEM image after ball milling [9]
2.3 Property Measurement Methods

Thermoelectric properties are difficult to measure accurately. Often they are measured independently of each other on different machines using different samples. Combined experimental error from the three measurements can easily dominate the results.

All of these measurements were confirmed by two independent techniques at both BC and MIT on more than 100 samples. The electrical conductivity was measured by a four-point current switching technique. The Seebeck coefficient was measured by a static DC method based on the slope of a voltage versus temperature-difference curve, using commercial equipment [14] on the same bar-type sample with a dimension of 2 mm by 2 mm in cross-section and 12 mm in length.

The thermal diffusivity $\alpha$, was measured by a laserflash method on a disk using a commercial system [15]. Thermal conductivity was calculated using the equation $k = \alpha \rho c_p$, where $\rho$ is the density and $c_p$ is the specific heat of the material which was measured using a differential scanning calorimeter [15].

2.4 Individual Property Data

Our nanocomposite properties were measured as a function of temperature by MIT and BC. Fig. 2.2 shows all the properties as a function of temperature including $ZT$, with a polynomial fitting curve which will be used later in the model.
Below is a table of the estimated uncertainty in each of our property measurements and the resulting average Gaussian uncertainty in ZT.

<table>
<thead>
<tr>
<th>Property</th>
<th>Instrument uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seebeck Coefficient</td>
<td>5%</td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>5%</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>8%</td>
</tr>
<tr>
<td>ZT</td>
<td>11.7%</td>
</tr>
</tbody>
</table>

An increase in ZT of 12% is significant; therefore it is undesirable to have an uncertainty of 12% in our measurement. The most convincing way to verify our high performance nanocomposite was to perform device tests on them. These are the most
conclusive tests because they essentially verify all the properties simultaneously. My lab mates Qing Hao and Austin Minnich performed a maximum ΔT cooling measurement while I designed and performed a novel power conversion measurement (Chapter 4). The energy conversion measurement system is designed to measure efficiency rather than ZT as a function of temperature; in fact ZT is only an indicator of performance because it is based on the constant properties model. Therefore it was necessary to use a temperature dependant model to predict conversion efficiency and verify our measured properties.
Chapter 3: Modeling Based On Temperature Dependent Properties

Thermoelectric properties are highly temperature dependent and every real material has an operating range around its peak $ZT$ value (Fig. 1.11). If a device is to operate over a large temperature range then more than one material system must be used. An efficiency model is needed that captures the temperature-temperature of the properties in different materials. Although $ZT$ is the best non-dimensional number the thermoelectric community has it is derived from the constant properties model and cannot precisely predict device performance over large temperature differences. In the case of our nanocomposite it would be very unclear what $ZT$ values to use since the properties may vary by a factor of 2 over the operating range (Fig. 2.2). This section will introduce a temperature dependent model used to predict power conversion efficiency.

3.1 Temperature Dependant Conversion Efficiency

The $\text{Bi}_2\text{Te}_3$ nanocomposite properties, $\rho(T), \kappa(T), \alpha(T)$ are a strong function of temperature so the typical $ZT$ efficiency Eq. 1.3.4 is not applicable. For this reason it is necessary to go back to the governing equation for thermoelectricity (Eq. 1.2.2) and keep the temperature dependence of the electrical resistivity, thermal conductivity and Seebeck coefficient. The following is a similarity solution to the governing equation of thermoelectricity, [2]

$$\frac{dY}{dT} = -T \frac{d\alpha}{dT} \frac{\rho \kappa}{Y} \quad (3.1.1)$$
where \( Y(T) \) is the similarity variable defined below.

\[
Y(T) = -\frac{\kappa dT}{J dx}
\]  

Eq. 3.1.1 is a 1\(^{st}\) order, nonlinear ODE, which can be solved for numerically with one boundary condition, \( Y(T_c, J) \) where \( T_c \) is the cold side temperature and \( J \) is the current density. This equation is solved by holding \( T_c \) constant to represent the cold side reservoir and sweeping the boundary condition \( Y(T_c, J) \) to find all possible solutions to \( Y(T) \), up to the desired hot side temperature \( T_H \). Each solution corresponds to a different current density condition because \( T_c \) is kept constant. In this way \( Y(T_c, J) \) has determined \( Y(T) \) and now the current density, load matching condition and efficiency are solved for.

\[
J = \frac{1}{L} \int_{T_c}^{T_H} \frac{\kappa dT}{Y} 
\]  

\[
M = \frac{R_{\text{Load}}}{R_{\text{internal}}} = \frac{\int_{T_c}^{T_H} \frac{\rho \kappa dT}{Y}}{\int_{T_c}^{T_H} \alpha dT} - 1
\]  

\[
\eta = 1 - \frac{Q_c}{Q_H} = 1 - \frac{Y(T_c) + T_c \alpha(T_c)}{Y(T_H) + T_H \alpha(T_H)}
\]

Alternatively the efficiency and heat transfers can be computed by a finite difference solution \([16,17]\). In this method the TE leg is subdivided into many small segments such that there is a small temperature difference across each segment and therefore the properties are considered constant. The details of the method can be found
in [2], and should yield that same results given a sufficient number of segments is used. The finite difference model is more attractive when considering a segmented leg (more than one material stacked in series).

The quantities defined in 3.1.3, 3.1.4 and 3.1.5 are important quantities that must be measured experimentally. The graphs to be generated experimentally will be efficiency versus current or load matching, and maximum efficiency versus temperature difference. The maximum efficiency is determined by finding the $Y(T_c, J)$ that yields the overall largest efficiency for a given $T_H$ and $T_C$ from Eq.3.1.5. Fig. 3.1 plots maximum efficiency vs. delta T for $T_C = 300[K]$. The temperature dependant curve is generated from Eq.3.1.5 given $T_H$ and $T_C$. The temperature independent curve was generated by fitting Eq.1.3.4 to the temperature dependant model data corresponding to $ZT = 1.27$. 
Figure 3.1: Maximum efficiency vs. $\Delta T$ for the temperature dependant model and a best fit $ZT=1.27$ model. Property data from previous section

In order to generate Fig. 3.1 the load matching condition which produces the maximum efficiency at a given temperature difference must be found. Figure 3.2 plots efficiency vs. resistance ratio, $M$ for both models (equations 1.3.2 and 3.1.4). Interestingly the peak efficiency occurs at nearly the same load matching and the curves are very similar except for an offset between them. The model results in the last two graphs will be compared to the experimental results in the next chapter.
There are two conclusions to be drawn from the last two graphs:

1) The temperature-dependent model is necessary to precisely verify thermoelectric properties over a large temperature range. For a material still under development where different techniques are being applied to enhance properties, the temperature-dependent model should be used to resolve these differences. If a TE material is to be used in a high performance application like the aerospace industry then most likely a temperature-dependent model will be necessary.

2) The constant ZT model is accurate enough for preliminary engineering of thermoelectric systems. If TE implementation is being considered in a
feasibility study or if the application doesn’t have very stringent constraints on performance, then an effective ZT model can be used.

In general, it is recommended to first use the temperature-dependent solution if the property data is available, since this method is not computationally expensive for a single leg. Next an effective ZT should be fit to the efficiency solution over the range of interest and the effective or average property values calculated. The temperature-dependent solution should be compared to the temperature-independent solution so uncertainty estimates can be calculated and then a decision can be made on which model to use. If property data is very limited then the constant properties model with a best fit effective ZT may be the only option.
Chapter 4: 1<sup>st</sup> Generation Efficiency Testing

The previous chapters have demonstrated that thermoelectric properties are highly temperature dependant and difficult to measure accurately. Since errors in individual property measurements compound to give larger error in power efficiency we decided to measure the power efficiency directly in order to characterize our material better. A power conversion measurement system was developed to better characterize our TE material by testing it under the same conditions as a real device. This system measures the performance of a TE material in the most direct way and will be used to evaluate the properties simultaneously as well as individually. Finally I will compare the experimental results with the model results from the property data in chapter 3.

Figure 4.1: Energy balance of a TE sample during the power conversion measurement
A power conversion measurement like this one requires all the elements of a real working device. The material must be in good thermal contact with a heat source and sink and must be electrically connected to an external circuit where the electrical power is dissipated, Fig. 4.1. Similar to a commercial TE module the leg needs to be soldered to electrical leads which are also good electrical conductors if a TE material is to be made into a device. The biggest different between a TE material and a device ready TE leg is a metalized layer on the ends that can be easily soldered to. The metalized layer is usually Ni and its purpose is to allow soldering with low electrical and thermal resistances and to act as a diffusion barrier to solder contamination. Since the material is a doped semiconductor the danger is that solder will diffuse into the sample and effectively dope it, and change the properties.

In the case of the nanocomposite a 12.5 µm thick Ni foil layer is attached to either end during hot pressing, Fig. 4.2 is a picture of a nanocomposite sample with Ni foil contacts. There is always an electrical contact resistance between the Ni layer and TE material, as well as a smaller thermal contact resistance. A thermal contact resistance will cause a temperature drop across the interface and decrease the maximum allowable Carnot efficiency. Electrical contact resistance decreases power output because there is a voltage drop across the interface and electrical power is dissipated as Joule heating. The presence of electrical contact resistance is an important distinction between a bare TE material and a device ready leg, the effects on overall performance will be seen later in the chapter.
The 1st generation of the power conversion measurement system was designed to measure the current flowing through the sample, the voltage across the sample as well as the cold side heat flux and temperatures. From these measurements one can solve for the conversion efficiency using

$$\eta = \frac{IV_{TE}}{Q_H} = \frac{IV_{TE}}{Q_C + IV_{TE}}$$ (4.0.1)

where \(I\) is the current, \(V_{TE}\) is the voltage across the sample/load resistance and \(Q_C\) is the cold side heat transfer measured by a heat flux sensor. In principle the measurement is simply performing an energy balance over the TE leg, in practice obtaining an accurate measurement of the above quantities can be challenging for the following reasons:

1) One should be careful when measuring \(Q_H\) or \(Q_C\) because the presence of unwanted modes of heat transfer can create a difference in heat transfer measured at the sensor to the actual heat transfer entering or exiting the sample. The heat flux sensor must be carefully designed and calibrated to account for this fact.
Air conduction and radiation occur at the heater, leg side walls, and heat flux sensor. When measuring a single leg it is easier to accurately measure the heat flux at the cold side rather than at the hot side because the temperature is closer to ambient and therefore thermal losses are lower. The presence of heat loss along the side walls of the sample suggests that a cold side heat flux measurement leads to an upper limit estimate for efficiency while a hot side heat flux measurement leads to a lower limit estimate for efficiency.

2) The thermovoltages and the electrical resistances of the sample are small which can lead to relatively large uncertainties in voltage if a high precision instrument is not used. Thermo-electrical voltage resolution on the order of 10µV is commonly needed in such experiments. A National Instruments SCXI conditioning box was used to measure all the voltages (<1 µV resolution) and thermocouples (<0.05°C resolution, ~.1°C accuracy). Precautions were also taken to reduce the RF noise in the electrical system such as shielding and soldered connections. The cryostat pressure vessel is made from aluminum construction and acts to shield the circuits inside from external noise, no AC currents where run inside the vessel, and shielded wires were used when ever possible outside the vessel. A type-K thermocouple wire feed thru was installed so that the thermocouple circuit was made entirely of thermocouple wire with no change in material. Originally the cryostat had a copper feed through that thermocouples wires were soldered to, this can give erroneous results due to a finite temperature drop across the feed though material.
3) Variation in sample properties and contact resistance are always present which make it hard to distinguish experimental error from an actual change in expected properties. For example, the hot pressed Ni foil sample electrical resistance can vary substantially depending on the hot pressing conditions. Attaching a Ni foil layer to the Bi₂Te₃ material with good mechanical strength and low electrical resistance presents significant challenges and it is a topic of ongoing research [9]. Many times during our experiments the Ni layer would detach during soldering making an efficiency measurement impossible or the contact resistance was found to be too high leading to poor efficiency. Additionally, the samples where cut into blocks and sometimes these blocks varied in cross section along its length which can lead to large uncertainties in the geometry.

4.1 Power Conversion Measurement System Design

The 1st generation power conversion measurement system was designed to measure the current, voltage across the sample and cold side heat flux and temperatures to solve for conversion efficiency by Eq. 4.0.1. A photo of the system with a sample mounted is shown in Fig. 4.3. A copper wire is soldered to the top of the sample which is maintained at \( T_H \) and conducts both the current and heat from the heater. A thermocouple soldered to the top of the sample measures \( T_H \) and acts as one of the two voltage probes. The bottom of the sample is soldered to a copper heat spreader maintained at \( T_C \). Mounted to the heat spreader is a cold side copper wire to complete the electrical circuit and a thermocouple which measures \( T_C \) and acts as the second voltage probe. The heat flux sensor is mounted to the bottom of the heat spreader and
measures $Q_c$ conducted across it. The heat sink for the heat flux sensor is the cryostat cold finger which is maintained lower than room temperature by chilled coolant (water and antifreeze) pumped through the cold finger. The electrical load resistance is controlled by two power MOSFETs[18]. A schematic representation of the thermo-electrical energy flow is given in Figure 4.4 where the heat transfers are depicted by red arrows and the electrical power is in green. Ideally there is no energy loss along the side walls of the leg and all the cold side heat is conducted across the heat flux sensor. Notice the heat loss from the surfaces and heat conduction loss and Joule heating and from the cold side electrical wire.

Figure 4.3: 1st generation power conversion measurement.
Figure 4.4: Schematic of energy flow within the system. The red arrows are heat transfers and the green arrows are energy flows from the electrical circuit.

The tests were conducted in a cryostat under a high vacuum (5x10^{-5} torr) to eliminate convection and reduce air conduction loss Fig. 4.5. In order to achieve lower pressure the chamber was modified so that the pump was connected to the bottom with a pressure gauge very close to the sample. Originally the pump was connected to a needle valve at the top of the chamber so there was a big pressure drop across that valve and down to the bottom of the chamber. Instead the valve was bypassed by attaching a custom made flange to a window at the bottom of the chamber near the sample. There is essentially no pressure drop from the bellow to the sample because there is no flow restriction. The pressure gauge was also moved from the turbo pump inlet to a location very close to the sample allowing an accurate pressure measurement.
The thermo-electrical circuit must satisfy three assumptions made by the model, which will be discussed later in detail:

1) Heat and current transport is one dimensional through the sample with no losses from the side walls. Top and bottom surfaces are isothermal

2) All the heat leaving the cold side is conducted through the heat flux sensor with negligible thermal losses.

3) There is no joule heating by the current carrying wire on the cold side.

The conditions above will be addressed individually in the next three sections; the challenges of meeting these conditions will be discussed and the solution will be presented.

**4.1.1 One Dimensional Flow**

The first condition is satisfied by choosing the right geometry and making a good solder contact. A good solder contact with relatively high thermal conductivity solder
can easily maintain a constant uniform temperature boundary condition. Choosing a sample that is cut well with a constant cross section will satisfy the 1-dimensional flow condition. Thermal losses along the sample walls are kept low by satisfying the following ratio.

\[
\frac{R_{\text{conduction}}}{R_{\text{convection}}} \ll 1 \tag{4.1.1}
\]

\[
\frac{UH^2}{4kA} \ll 1 \tag{4.1.2}
\]

where \( H \) is the height of the leg and \( U \) is the overall heat transfer coefficient of the surface. A short, wide leg will have relatively less losses from the surface, the ratio above was typically around 0.03 (cubic sample, 2mm per side, \( U=15 \) [W/m\(^2\)K]) so that side wall losses where minor and could be neglected in the analysis. The measurements were performed in vacuum at 5x10\(^{-5}\) Torr in order to reduce convection and air conduction losses.

The solder was chosen based on the convenience of the melting temperature. Most solders have a thermal conductivity around 35 [W/mK] and electrical resistivities around 10\(^{-7}\) [\(\Omega\)m] while Bi\(_2\)Te\(_3\) is around 1 and 10\(^{-5}\) respectively. Therefore isothermal boundary conditions with no bulk solder resistance are good assumptions. The electrical contact resistance between solder and other metals (Ni, Cu) is negligible; it is the contact resistance between the nickel layer and the bulk sample that dominates. Low temperature 120°C solder was used on the cold side to prevent thermal damage to the heat flux sensor. On the hot side 234°C solder was used because this corresponds
closely to the maximum operating temperature of our Bi$_2$Te$_3$ nanocomposite. Thermocouples were soldered directly with the use of solder flux.

4.1.2 Thermal Circuit

The second and third conditions are more challenging to satisfy. The majority of the cold side heat transfer must be conducted through the thermopile type heat flux sensor. Any thermal losses due to air conduction, radiation and conduction along the cold side electrical wire will lead to a smaller measured heat transfer than the actual; therefore the thermal resistance of the heat flux sensor should be much smaller than the others. The thermal circuit is given in Fig. 4.6; $Q_C$ enters the copper heat spreader at the blue node; the majority of the heat is conducted across the sensor resistance which has two interface resistances in series with it. Radiation shielding was used to increase the convection and radiation resistance communicating with the green node at room temperature. $R_{\text{WIRE}}$ is a conduction resistance to the cold finger temperature (yellow node) from the copper current carrying wire on the cold side.
The only way to account for the additional thermal losses was to calibrate the heat flux sensor. Fig. 4.7 shows a schematic of the calibration procedure with all modes of heat transfer and relevant thermal resistances. The copper spreader resistance $R_{\text{Spreader}}$ is two orders of magnitude smaller than $R_{\text{SENSOR}}$, so the copper spreader temperature $T_C$ can be considered uniform. The largest heat loss at the flux meter is from conduction along the cold side current carrying wire which has a calculated thermal resistance of 149 [K/W]. Heat loss by radiation has a higher thermal resistance, calculated to be 5390. The sensor itself, including contact resistances has a measured resistance of 15.5, therefore combined thermal losses should constitute about 9.7 % of the actual $Q_C$ entering the copper heat spreader.
During heat sensor calibration a 20 Ohm heater was attached to the copper spreader without the top copper wire present. The heater power entering the copper spreader was calculated by knowing the heater current and heater resistance (the change in heater resistance with temperature was found to be negligible). Figure 4.8 plots the measured heat flux versus time, this data was used to find the heater power to voltage proportionality constant. A linear relation for electrical heater power to voltage output was determined to be 0.139 [W/mV] which would be used for the rest of the measurements. This is the same proportionality constant given by the manufacturer for thermal radiation measurements. The manufacture’s calibration was done by a proprietary conduction method and has an accuracy of 3% [19]. The fact that the proportionality constants are the same suggests that the heat loss from the cold side wire
is smaller than expected. Figure 4.9 plots the heater power to measured power ratio at slightly different calibration conditions (temperature, pressure, heater current). From the results of this graph, it is estimated that uncertainty in the cold side heat transfer measurement is about 4%.

Figure 4.8: Heat flux sensor calibration curves, $Q_c$ versus time

Figure 4.9: Actual heater power to measured power ratio vs. time. This gives an uncertainty estimate for the heat flux sensor.
4.1.3 Electrical Circuit

The 2\textsuperscript{nd} and 3\textsuperscript{rd} assumptions conflict because thermally a thin wire is desired to reduce conduction losses while electrically, a thicker wire will reduce Joule heating. The final wire had an electrical resistance of 1mΩ. It is expected that approximately half of the joule heating through that wire is expected to enter the flux sensor while the other half would be conducted to the cold finger. Therefore a current of 2 A will contribute 2 mW ($I^2R/2$) of heat to the flux sensor.

The current flow is generated by the TE leg and is dissipated in the load matched resistor. Finding an adjustable resistor was a challenge. The sample resistance was typically around 5-10mΩ it is not possible to buy a potentiometer that operates in this range with a sub 1mΩ resolution. The solution is to use power MOSFETs as controllable resistors by adjusting the gate voltage [18]. Usually MOSFETs are operated like switches where a zero gate voltage is an open circuit (10MΩ) and 10 volts to the gate is a closed circuit (<2mΩ). However for intermediate gate voltages you get a continuous change in resistance that can be controlled precisely [18].

Two power MOSFETS where used in series with the sample, Figure 4.10 shows a schematic of the electrical circuit procedure of the current measurement. The procedure was to open one of the MOSFETS (0 gate voltage), apply a constant gate voltage to the second MOSFET and measure the four wire resistance of the second MOSFET. Now that the resistance is known the first MOSFET was closed (10 volts to gate) and the current is solved by dividing the voltage drop across the second MOSFET by the previously measured resistance. In this way the second MOSFET operates as a variable load resistance and current sense resistor. The minimum load resistance of the entire
external circuit was about 6 [mΩ], this includes the copper wire connections and both MOSFETs at their minimum resistance.

![Electric circuit diagram](image)

**Figure 4.10: Electric circuit and load matching procedure.**

### 4.2 Individual Properties Measurements

It is possible with the system presented to make independent measurements of the electrical conductivity, Seebeck coefficient and thermal conductivity as a function of temperature.

The temperature dependent thermal conductivity can be verified by measuring $Q_C$ when a temperature gradient is imposed with no current flowing. The cold side heat
transfer measured by the flux sensor is a function of the thermal conductivity of the material and the geometry and temperatures.

\[ Q_c = \frac{A}{L} \int_{r_c}^{r_h} k(T) dT \]  \hspace{1cm} (4.2.1)

The Seebeck coefficient is verified by measuring the Seebeck voltage at the same conditions: temperature gradient present and no current flowing. The Seebeck voltage is measured between the alumel thermocouple wires on the hot side and cold side; the Seebeck voltage of the sample is the equal to the total voltage minus the Seebeck voltage of the alumel wires. The Seebeck voltage of the sample is a function of the Seebeck coefficient and the temperatures on either end.

\[ V_{\text{Seebeck}} = \int_{r_c}^{r_h} \alpha(T) dT \]  \hspace{1cm} (4.2.2)

The electrical resistivity is verified by measuring the total resistance of the sample when a temperature gradient is present and no current is flowing. The total sample resistance includes the bulk resistance and contact resistance and is measured by applying a small alternating DC voltage at 20 Hz and measuring the amplitude of the voltage across the alumel thermocouple wires. The alternating current assures that any Seebeck voltages will be canceled out, and the frequency is high enough that the temperatures at the end of the sample remain approximately constant. The alternating DC labview program was written in such that the frequency can be controlled, if the frequency is not high enough then the voltage of the leg will have a linear slope with time. In this case the frequency was increased until this effect was no longer present. The total sample resistance is calculated by the following expression
\[ R = \frac{V_{AC}}{I_{AC}} = \frac{L}{A} \int_{T_c}^{T_H} \rho k dT + R_C(T_c) + R_C(T_H) \]  

(4.2.3)

where \( R_C(T_H) \) and \( R_C(T_C) \) are the contact resistances on the hot side and cold side respectively.

### 4.3 Results and Analysis

The power conversion measurement system was used to measure the efficiency of our Bi\(_2\)Te\(_3\) P-type nanocomposite samples as well as a commercial leg. The commercial samples represent the standard commercially available Bi\(_2\)Te\(_3\) thermoelectrics and in fact the nanocomposite raw material was purchased from the same supplier. This direct comparison between the commercial Bi\(_2\)Te\(_3\) and the nanocomposite allows for evaluation of the commercial viability of our nanocomposite method since both samples came from the same raw material. Fig. 4.11 shows the efficiency results from measurements using the first generation system. The nanocomposite efficiency is plotted with the raw load matching data included while only the peak commercial leg efficiency data is plotted.

The last temperature point in Fig. 4.11 is circled and plotted again in Fig. 4.12 to show the load matching condition. Fig. 4.12 plots efficiency versus current as an example of the load matching procedure that must be done for each temperature point. The blue points are experimentally measured and the pink curve corresponds to \( ZT=0.786 \) and a sample resistance of 8.7 m\( \Omega \) using Eq.1.3.2. From this graph it is clear that the resolution and repeatability of the measurement is good because the load matching condition is captured with fine detail. Ideally the different load matching
conditions would all occur at the same temperature points but this is not practical because this would require changing the heater power for each change in current.

Figure 4.11: Efficiency vs. deltaT for measured and model results. The BT P-type nanocomposite is plotted in blue and the commercial P and N types are plotted in pink and yellow.
Figure 4.12: Efficiency vs. current around 200 delta T, experimental points are in blue, the pink curve corresponds to ZT=0.786 and Rsample=8.7 mΩ

From comparing the nanocomposite to the commercial legs it is clear that our material has higher efficiency everywhere. Also it was observed that the nanocomposite had better temperature stability because there was one occasion that solder diffused and destroyed one of the commercial samples around 200°C. Based on comparing the morphology of the damaged commercial sample to photographs in the literature it was determined that diffusion of solder lead to failure. Over the time span of 10 hours the commercial sample efficiency degraded to near zero. The sample had grown whisker like crystals structures along the side walls due to the alloy separating into phases, Fig.
4.13. For this reason the commercial samples were not taken to 200°C. Even though
the nanocomposite is made of small grains that may sinter together at elevated
temperature the abundance of grains boundaries and the high packing density probably
slows mass diffusion and protects against solder diffusion [9].

Fig. 4.11 also plots the model results for the nanocomposite which do not agree
good with experiment. The source of the discrepancy between the model and experiment
could not be easily traced to measurement error so the system was adapted to measure the
individual properties independently instead of relying on the previous data from BC.
The previous was compiled from the bulk properties of many samples without hot
pressed Ni foil. It’s well known that this material system is sensitive to the hot pressing
conditions so it is reasonable to question whether the Ni foil-Bi$_2$Te$_3$ system is different from the original.

Table 2 gives the measured electrical resistance of the P-type nanocomposite with Ni plating versus the calculated electrical resistance based on Eq. 4.2.3. The electrical resistance of the sample was measured at different temperature gradients and the difference between the predicted electrical resistance (using $k, \rho$ property data from chapter 2) and the measured was found to be small so it was not necessary to modify the resistivity data or include an electrical contact resistance correction.

<table>
<thead>
<tr>
<th>Delta T</th>
<th>$R_{\text{measured}}$ [mΩ]</th>
<th>$R_{\text{calculated}}$ [mΩ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>88.31</td>
<td>3.435</td>
<td>3.430</td>
</tr>
<tr>
<td>88.38</td>
<td>3.433</td>
<td>3.430</td>
</tr>
<tr>
<td>156.96</td>
<td>4.159</td>
<td>4.161</td>
</tr>
</tbody>
</table>

Table 2: Electrical resistance, measured and calculated for different temperature differences

However it was found that the other two properties needed to be modified. The thermal conductivity was measured again on the laser flash system with a Ni coated sample and found to be 10-15% higher everywhere; Figure 4.14 plots the new temperature dependence of $k(T)$ compared to the bare nanocomposite values. The experimental Seebeck voltage is compared to the calculated Seebeck voltage (Eq. 4.2.2) from the measured bulk values in Fig. 4.15. The measured Seebeck voltage was found to be about 8% lower than predicted, so the temperature dependant Seebeck coefficient of the Bi$_2$Te$_3$-Ni foil system was reduced by 8% for all temperatures.
Figure 4.14: Thermal conductivity vs. temperature for nanocomposite with and without Ni foil.

Figure 4.15: Seebeck voltage vs. temperature difference, the measured and model predictions are plotted.

It is evident from the Seebeck coefficient and thermal conductivity that the nanocomposite-Ni foil properties are different from the nanocomposite alone. There are a few possible reasons for the degradation in properties:

1) Ni foil has either doped or alloyed with the Bi₂Te₃ material
2) The hot pressing temperatures at the boundaries have increased due to electrical resistance at the Ni foil interfaces.

3) The Ni foil may have changed the current distribution in the powder during hot pressing which in turn has changed the properties.

The model was updated with the degraded properties of the Bi$_2$Te$_3$-Ni foil system as just described. The latest model uses the original electrical resistivity data with no contact resistance correction, a new temperature dependant Seebeck coefficient (8% lower) and the new thermal conductivity from Fig. 14.

Fig. 4.16 shows the efficiency results compared to the updated model with modified properties. The predicted model results now match closely with experiment with a difference of about 5%. The efficiency results are close enough that the load matching conditions can now be plotted on the same graph, Fig. 4.17. The load matching curves are similar except for a 5% offset, and the currents corresponding to a maximum in efficiency are very close for both the experimental and new model curves.
Figure 4.16: Efficiency vs. delta T for updated model results and measured nanocomposite

Figure 4.17: Efficiency vs. current around 200 delta T. Updated model curve in pink, Experimental curve in blue.
Chapter 5: Conclusions and Future Work

5.1 Summary and Conclusions

A high performance thermoelectric nanocomposite has been developed and tested by groups at MIT and BC. The nanocomposite is a P-type Bi$_2$Te$_3$ alloy with nanosized grains that can be made in large quantities [9]. It has an operating temperature range around room temperature which makes it an ideal TE material for refrigeration and waste heat recovery applications.

The nanocomposite properties had previously been measured by both groups at MIT and BC and it was known to have a high ZT. However measuring the properties independently can accumulate significant error in ZT so it was decided that a direct power conversion efficiency measurement was needed to better characterize the material.

In this work, it was shown that a temperature-dependant property model is necessary to accurately predict the conversion efficiency of a real TE material. The system that was developed can measure individual temperature dependant properties or the power conversion efficiency directly. The temperature dependent model agrees well (within 5%) with experiment when the Bi$_2$Te$_3$ nanocomposite-Ni foil properties (Seebeck coefficient, electrical resistivity, thermal conductivity) are used.

The nanocomposite power conversion efficiency is clearly better than the commercial samples at all temperatures. Preliminary observations also show that the nanocomposite structure has better resistance to solder diffusion damage. However the efficiency of the Ni foil- Bi$_2$Te$_3$ system is still significantly lower than the originally
predicted nanocomposite efficiency without Ni foil. It’s clear that the nanocomposite-Ni foil efficiency can be improved beyond its current value.

The power conversion measurement system developed in this work has proven a valuable tool for characterizing the nanocomposite-Ni foil system and has identified differences between the nanocomposite with the Ni foil and with out. The Ni metalized layer is a necessary component in all TE devices; it is not just the TE material that is important but the TE-contact system. Attaching the Ni foil without affecting other properties and adding large contact resistance is still an area of active research. Through this work, the nanocomposite has progressed from a high ZT material with independently measured properties, to a high performance real working TE device that challenges the commercial standard Bi$_2$Te$_3$ bulk alloy.

5.2 Future Work: 2$^{nd}$ Generation Efficiency Testing

After the success of the first generation efficiency measurement system is was decided that we will continue to measure efficiency of our TE materials. A second generation system is currently being designed with aims to increase measurement accuracy and increase throughput. This system should also be capable of testing high temperature SiGe samples at hot side temperatures up to 1000°C.

The 2$^{nd}$ generation power conversion measurement uses a similar general design, but improves on the electrical and thermal circuit. Fig. 5.1 shows a picture of the new system during the heat flux sensor calibration.
Electrically, the two MOSFET have been replaced by a current source. This simplifies the circuit and circumvents the load matching problem because now only a current needs to be supplied. The hot side current carrying wire can be much smaller because it will not change the load matching condition. This means that the heater power is smaller and the cold finger experiences less heat load. More precise control of the current and less heater power allows the system to come to steady state more rapidly. The current source also allows the possibility of testing under heat pump conditions of very high current.

Thermally the second generation system has a few new features. One is that the new heat flux sensor is much smaller with $\frac{1}{4}$ the area and $\frac{1}{2}$ the thermal resistance. Other advancements are that a TE cooling module has been added to control the copper block temperature and the cold finger temperature is actively controlled. This allows the copper heat spreader and everything else it communicates with to be kept at room temperature (\(+0.25\text{C}\)) except the bottom of the heat flux sensor which is below room temperature (Fig. 5.2).
Figure 5.1 2nd generation thermal circuit from the copper spreader, the green nodes kept at room temp. and the yellow node is kept below room temp by the TE cooler

A thicker electrical wire has been used to decrease the effects of Joule heating. Normally this would mean more heat conduction loss; however, the TE cooler maintains the copper spreader at ambient to minimize heat transfer losses. Therefore the new thermal circuit in Fig. 5.2 has more favorable thermal resistances with nodes at controlled temperatures. For instance the old system might have a temperature drop of 7.5 C across the flux sensor and cold side electrical wire. Now at the same $Q_C$ I have a temperature drop of 3.5 C across the flux sensor and 0.3 C across the cold side electrical wire. Thus the relative heat losses are kept significantly lower.
References

2. Rowe, D. M. *Handbook of Thermoelectrics* (CRC Press, 2006)


