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### 36-SAMPLE MEASUREMENT SYSTEM FOR DOPING AND ALLOYING TRENDS IN NEW THERMOELECTRIC MATERIALS

By

Sim Yean Loo

### A THESIS

Submitted to Michigan State University In partial fulfillment of the requirements For the degree of

### MASTER OF SCIENCE

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#### ABSTRACT

# 36-SAMPLE MEASUREMENT SYSTEM FOR DOPING AND ALLOYING TRENDS IN NEW THERMOELECTRIC MATERIALS

By

Sim Yean Loo

A computer-control high sample throughput thermoelectric measurement system is presented in this thesis. The system is designed to measure 36 samples simultaneously in a single temperature run (4.2K - 400K) for thermoelectric characterization. Thermoelectric power is being investigated since it has the largest influence on the thermoelectric efficiency of a sample. The purpose of this system is to study doping and alloying trends in new thermoelectric materials in a high-throughput manner.

The system set-up and wiring process are included in this document. It further provides valuable technical information for system utilization. Many significant features of the system, including computercontrol, easy sample mounting, and high sample throughput have made it a unique system for characterizing thermoelectric materials. Results of the characterization have been compared to the standard reference data showing good agreement. Some problems are addressed in this paper and suggestions for improvements are given. Dedicated to my parents

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#### Introduction

As science has developed and the human's life is getting more comfortable than ever, are there still ways to further improve the existing living style? The answer is always yes. At home, a refrigerator compresses and condenses a gas (often a chlorofluorocarbon) to maintain a cold environment for storing food; an air-conditioner is ready to output cold air when it is turned on and a car is prepared for transporting from one place to another. However, all these "household" items have their own disadvantages that people may or may not realize. Possible improvements include quiet and robust refrigerators that do not produce environmentally harmful gases, microprocessors able to run at increased speeds, and a car that can convert the waste heat generated by the engines into usable power.

The discovery of thermoelectric effects has made a big impact on these issues. The robustness and high reliability of a thermoelectric (TE) device, due to its solid-state construction, allows it to be operated under harsh conditions, for instance under vibration. In addition, its scalability has made it available to meet strict application requirements. For instance, a TE device can be miniaturized to meet compact design constraints. Thermoelectric devices have no moving parts and are virtually maintenance free. They can be used in any orientation and in

zero gravity environments. Thus, many have been used in aerospace application [1].

Scientists have been creating and trying new thermoelectric materials over many years toward the goal of more efficient energy conversion. This has been a challenging endeavor as indicated in the dominance by a single material (Bi<sub>2</sub>Te<sub>3</sub>) for near room temperature applications for over forty years. The greatest cooling efficiency comes from thermoelectric materials that conduct electricity well but are poor heat conductors. Unfortunately, there are very few materials that fall into this category, however recent studies have shown that more investigations are needed to understand the limits in the thermoelectric field [2, 3]. Bismuth telluride, Bi<sub>2</sub>Te<sub>3</sub>, was introduced in 1954 [4] and today can be found in portable beverage coolers that plug into a car's cigarette lighter. However, the cooling efficiency and the cost have made thermoelectric devices less competitive than their compressor based counterparts.

The unitless figure of merit, ZT, combines a material's electric and thermal conductivities with a measure of its capacity to generate electricity from heat, and as will be shown, represents a material's potential in thermoelectric use. After almost 46 years of searching, Bi<sub>2</sub>Te<sub>3</sub> still has the highest ZT. The figure of merit is a temperature dependent property which peaks at ~1 for Bi<sub>2</sub>Te<sub>3</sub> near 300K. For a thermoelectric material to come close to replacing the compressor-based refrigerator

near room temperature, it would need a ZT of 4 or 5. Predictions for the use of thermoelectric systems in automobiles suggest ZT's of at least 2 are needed [5].

Besides Bi<sub>2</sub>Te<sub>3</sub>, lead telluride and silicon-germaium alloys had been used during the early years of research. Lead telluride operates well at high temperature, about 427 C, making it better for power generation. While silicon-germaium alloys function well at very high temperatures about 727 C, e.g. Voyager spacecraft launched in 1977 used this material heated by radioactive sources as a power supply [6]. After a quarter of a billion device hours, not one of the 1,200 thermoelectric generators on each Voyager has failed [7]. It has thus, proved the robustness of thermoelectric device.

Below are the top performance of the most widely used materials for thermoelectric applications:

	Z <sub>max</sub> (K <sup>-1</sup> )	Useful Range	T <sub>max</sub> (K)
Bi <sub>2</sub> Te <sub>3</sub>	3x10 <sup>-3</sup>	< 500 K	300
PbTe	1.7x10 <sup>-3</sup>	< 900 K	650
Si-Ge	1x10 <sup>-3</sup>	< 1300 K	1100

Table 1.1 Most widely used TE materials' top performance

In 1993, it was shown that ZT greater than 1 in quantum well structures were possible [8]. This renewed interest in the field of thermoelectrics and has recently produced new avenues of research in thermoelectric quantum structures and new bulk materials.

In the process of making new materials, chemists are very naturally playing an important role. A group of researchers from the Chemistry Department at Michigan State University has been notably active in thermoelectric materials research. The polychalcogenide flux technique, they developed, allows them to investigate new materials in an exploratory synthetic approach [9, 10, 11]. After a promising material has been identified, it can then be more rapidly fabricated through a flash synthesis. More detail explanation of these material preparation techniques will be included later in this document.

The rate of sample production with flash synthesis can approach 100 samples per week per investigator. To accommodate such a high rate, a measurement system has been built with a high sample throughput. It is used to screen through samples and to determine general trends in doping and alloying variations. This high throughput measurement system is the focus of this thesis [12].

The figure of merit is most heavily dependent on the thermoelectric power (also commonly known as thermopower, or absolute Seebeck coefficient). If the thermopower of a sample is not promising, or cannot be maximized to a desired value, then the sample is not a likely candidate for thermoelectric applications. Thus the high throughput system described in this thesis has been designed to measure

temperature dependent thermopower of 36 samples in a single measurement run. In this way, we can focus our work on the most promising materials.

The paper will present the multisample measurement system. It will first describe the theories and history background. Next, the experimental setup will be shown. Then, system testing and actual data collection (result) will be explained. Discussions and analysis of the result will come before the further improvements and conclusion.



#### History background and theories

#### **2.1 Introduction**

In early 19th century, Thomas Seebeck and Jean Peltier, first discovered the phenomena that are the basis of the thermoelectric effects. In 1821, Seebeck found that an electrical current would flow if a temperature gradient builds up across the junctions of two dissimilar conductors connected as shown in Figure 2.1. Thirteen years later, Peltier learned that passing current through two dissimilar electrical conductors, caused the absorption or generation of heat at the junction depending on the direction of current, i.e. one junction is cold while the other is hot.

Thomson, who was later called Lord Kelvin, realized that there must be a relationship between Seebeck and Peltier effects and proceeded to derive the relation. This led him to conclude that a heating or cooling effect occurs in a homogeneous conductor when an electric current passes in the direction of a temperature gradient. This is called the Thomson effect, which completes the three fundamental thermoelectric effects [13, 14].

The most common thermoelectric device is a thermocouple. Thermocouple is made up of dissimilar materials, usually metals, with an electrical joint between the two materials. It utilizes the Seebeck effect, and is typically used for measuring temperature gradients. Other

applications of thermoelectric materials have included generators and coolers. Altenkirch first derived the basis theory of thermoelectric generators and refrigerators in 1909 and 1911. His theory has shown the challenging part of fabricating such devices with common materials is that the Peltier cooling is often much less than the Joule heating, which makes it difficult to utilize the Peltier effect. Furthermore, it was found that the heat conducted from the hot junctions to the cold junctions becomes excessive for thermocouples with short length and large crosssection area (i.e. large thermal conductance). Thus, a compromise must be made between reducing electrical resistance and increasing thermal resistance. Semiconductors have been found to make the most efficient thermoelectric generators and refrigerators. For both applications, materials with high thermoelectric power, high electrical conductivities (to minimize Joule heating), and low thermal conductivities (to minimize heat transfer losses) are required [15, 16, 17].

#### 2.1.1 Basic theories

To further discuss the thermoelectric theory, we should consider Kelvin relations and their derivation. Kelvin relations are the relationships of Seebeck effect with Peltier and Thomson effects. The relation between Seebeck and Peltier effects is very important because absolute Seebeck coefficient (also known as the thermoelectric power, i.e. thermopower, or thermal e.m.f. coefficient) which is most easily

measured, and Peltier coefficient which determines the cooling capacity of a thermoelectric refrigerator.



Figure 2.1 Closed circuit Seebeck Effect.

From Seebeck effect, in Figure 2.1, a current, I, flows in the circuit when a temperature difference,  $\Delta T$ , is created. The force that drives this current can be measured by breaking the circuit and measuring the voltage,  $\Delta V$ , with no current flowing as shown in Figure 2.2. The relative Seebeck coefficient is defined as the instantaneous rate of change of the relative Seebeck effect with respect to temperature at a given temperature. Thus, the relative Seebeck coefficient is

$$S_{AB} = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T}$$
(1)

Since the Seebeck effect shows that thermoelectric circuit converts thermal energy into electrical energy, its most common application is in thermometry. Thermocouples, which are typically composed of standardized metallic conductors, are used for accurate, sensitive, and reliable measurements.



Figure 2.2 Open circuit Seebeck Effect.

If in Figure 2.2 a current was forced to flow by placing a battery across the open terminals, then heat would be absorbed at one junction, and liberated at the other. This describes the Peltier effect which shows that reversible heat generation Q is established when a current, *I*, flows through a junction between the conductors A and B. This heat absorption (or generation) is a result of the change in entropy of the electrical charge carriers as they cross a junction. This heat pumping also occurs within nonhomogeneous conductor at concentration gradients or at phase interfaces within multiphase materials. The Peltier coefficient,

$$\Pi_{AB} = \frac{Q}{I} \tag{2}$$

is the change in the reversible heat content at the junction of conductors A and B when unit current flows across it in unit time, where  $\Pi_{AB} = \Pi_B - \Pi_A$  and,  $\Pi_A$  and  $\Pi_B$  are the respective absolute Peltier coefficients of the conductors. The direction in which current flows across a junction and the values of  $\Pi_A$  and  $\Pi_B$  determine whether heat is liberated or absorbed. For a constant current, the Peltier effect is proportional to the relative Seebeck coefficient, and at any fixed junction temperature, it is proportional to the current. These reversible effects are independent of the shape or dimensions of the junction. This is in contrast to Joule heating, which is a function of dimensions, does not require a junction, or change its sign, and is irreversible. Applications of the Peltier effect include thermoelectric devices for refrigeration and for power generation.



Figure 2.3 Thomson Effect.

The Thomson effect is the reversible change of heat content within any single homogeneous conductor in a temperature gradient when an electric current passes through it. This may occur in any nonisothermal segment of a conductor. The Thomson coefficient is the reversible change of the heat content within a single conductor per unit temperature gradient per unit current flow. The Thomson effect is a manifestation of the direction of flow of electrical carriers with respect to a temperature gradient within a conductor. If current flows in opposite direction to a thermal gradient, electrons gain potential energy. Likewise, if current flows in same direction as a thermal gradient, the potential energy of the electrons is reduced. Figure 2.3 shows that the passage of a current, *I*, along a portion of a single homogeneous conductor, over which there is a temperature difference  $\Delta T$ , leads to rate of reversible heat generation  $\Delta Q$ [13]. The Thomson coefficient is,

$$\gamma = \lim_{\Delta T \to 0} \frac{\Delta Q}{I \Delta T}$$
(3)

#### 2.1.2 Derivation of the formulas

The Kelvin relations may be derived by applying the laws of thermodynamics (First Law of Thermodynamics, i.e. energy is always conserved) to the simple circuit shown in Figure 2.4. A current, *I*, passes through this circuit, which consists of conductors A and B with junctions at temperatures  $T_1$  (colder junction) and  $T_2$  (hotter junction). Let  $T_1=T$  and  $T_2=T+\Delta T$ . From the principle of the conservation of energy, the heat generated must be equal to the consumption of electrical energy. If the current is small enough, Joule heating may be neglected. The relative Seebeck effect generated by the temperature difference is  $E_{AB}$ . The relative Seebeck coefficient is  $dE_{AB}/dT$  or  $S_{AB}$  so the electrical energy is expressed as

$$IE_{AB} = I \frac{dE_{AB}}{dT} \Delta T \tag{4}$$

For unit current flow through the circuit,

$$E_{AB} = \frac{dE_{AB}}{dT} \Delta T = S_{AB} (\Delta T)$$
(5)

The expressions for Peltier effect at the junctions are:  $\Pi_{AB}(T+\Delta T)$  for heat absorbed at the hotter junction, and  $-\Pi_{AB}(T)$  for heat liberated at the

colder junction. The expressions for Thomson effect within the conductors are  $\gamma_B(\Delta T)$  and  $-\gamma_A(\Delta T)$  for heat absorbed in conductor B and heat liberated in conductor A respectively [14]. Equating the heat generated to the consumption of electrical energy for unit current flow in the circuit gives

$$S_{AB}(\Delta T) = \prod_{AB} (T + \Delta T) - \prod_{AB} (T) + (\gamma_B - \gamma_A) \Delta T$$
(6)

Dividing by  $\Delta T$ , we get

$$S_{AB} = \frac{\prod_{AB} (T + \Delta T) - \prod_{AB} (T)}{\Delta T} + (\gamma_B - \gamma_A)$$
(7)

If assume  $\Delta T$  approaches zero, Equation 7 can be expressed as

$$S_{AB} = \frac{d\Pi_{AB}}{dT} + (\gamma_B - \gamma_A)$$
(8)

This is the fundamental thermodynamic theorem for closed thermoelectric circuits; it shows the energy relationship between the electrical Seebeck effect and the thermal Peltier and Thomson effects. It must be emphasized that Equation 8 is derived for closed circuits with no external electrical sources.



Figure 2.4 Closed TE circuit

The thermoelectric effects are actually irreversible because of the Joule heating and heat conduction. However, if we consider the thermal losses and electrical resistance of the thermoelement to be very small, we can neglect the irreversible heat loss and assume the TE circuit is thermodynamically reversible. Thus, the net change in the entropy,  $\Delta P$  can be assumed zero.

This gives

$$\Delta P \cong \frac{-\prod_{AB} (T + \Delta T)}{T + \Delta T} + \frac{\prod_{AB} (T)}{T} - \frac{\gamma_B (\Delta T)}{T + \frac{\Delta T}{2}} + \frac{\gamma_A (\Delta T)}{T + \frac{\Delta T}{2}} = 0$$
(9)

The first two terms of the Equation 9 can be multiplied by  $\Delta T/\Delta T$  to give

$$\Delta P \cong \left[\frac{\frac{-\Pi_{AB}(T + \Delta T)}{T + \Delta T} + \frac{\Pi_{AB}(T)}{T}}{\Delta T}\right] \Delta T - \frac{\gamma_B(\Delta T)}{T + \frac{\Delta T}{2}} + \frac{\gamma_A(\Delta T)}{T + \frac{\Delta T}{2}} = 0 \quad (10)$$

As  $\Delta T$  approaches zero the difference quotient within the brackets can be

replaced by  $-\frac{d}{dT}\left(\frac{\prod_{AB}}{T}\right)$ , so Equation 10 becomes

$$\Delta \mathbf{P} \cong -\frac{d}{dT} \left( \frac{\Pi_{AB}}{T} \right) \Delta T - \frac{\gamma_B (\Delta T)}{T + \frac{\Delta T}{2}} + \frac{\gamma_A (\Delta T)}{T + \frac{\Delta T}{2}} = 0$$
(11)

If assume  $\Delta T$  is very small, then  $T + \Delta T/2 \cong T$ . This gives a more simple equation

$$\frac{d}{dT}\left(\frac{\Pi_{AB}}{T}\right) \cong \frac{\gamma_A}{T} - \frac{\gamma_B}{T}$$
(12)

The indicated derivative reduces Equation 12 to

$$\frac{T\frac{d\Pi_{AB}}{dT} - \Pi_{AB}}{T^2} \cong \frac{\gamma_A}{T} - \frac{\gamma_B}{T}$$
(13)

which simplifies to

$$\frac{\prod_{AB}}{T} \cong \frac{d\prod_{AB}}{dT} + \gamma_B - \gamma_A \tag{14}$$

Equation 14 represents the entropy change at a thermoelectric junction in a closed circuit because  $\Pi_{AB}$  is the change in the heat content of the junction, and divided by the absolute temperature, is (by the Nernst definition) the change in entropy of the junction for the given temperature. From Equation 14, we can rearrange it for the selection of materials for use in Peltier devices,

$$-\frac{d\Pi_{AB}}{dT} \cong -\frac{\Pi_{AB}}{T} + (\gamma_B - \gamma_A)$$
(15)

To get the maximum Peltier effect, we set  $d\Pi_{AB}/dT = 0$ . This is used to obtained the optimum relationship between the two thermal effects as

$$\Pi_{AB} \cong (\gamma_B - \gamma_A)T \qquad (16)$$

Also, when  $d\Pi_{AB}/dT = 0$  is applied to Equation 8 we get

$$S_{AB} = (\gamma_B - \gamma_A)$$

So, Equation 16 becomes

$$\Pi_{AB} \cong S_{AB}T \tag{18}$$

Note that,  $S_{AB} = S_B - S_A$ 

Equation 18 is the first Kelvin relation. This equation is very helpful in understanding the operation of Peltier devices. It shows why combinations of thermoelements with large Peltier effects must be used for power generation or for refrigeration.

In order to derive the second Kelvin relation, take the differentiation of Equation 18.

$$\frac{d\Pi_{AB}}{dT} \cong S_{AB} + T \frac{dS_{AB}}{dT}$$
(19)

from Equation 8 to give

$$\frac{d\Pi_{AB}}{dT} \cong S_{AB} - (\gamma_B - \gamma_A)$$
<sup>(20)</sup>

Equation 19 and Equation 20 are then equated to get

$$T\frac{dS_{AB}}{dT} \equiv -(\gamma_B - \gamma_A)$$
(21)

rewrite it to

$$\frac{dS_{AB}}{dT} \cong \frac{(\gamma_A - \gamma_B)}{T}$$
(22)

Equation 22 is the second Kelvin relation.

Generally, both of Kelvin's relations are applicable to all the materials used in thermoelectric applications though there is an exception, germanium-copper couple. It appears that the value of the Peltier coefficient is less than the product of Seebeck coefficient and temperature.

Seebeck and Peltier coefficients are both defined for junctions between two conductors while the Thomson coefficient is defined for a single conductor. We can use Equation 22 to derive the absolute Seebeck coefficient for a single material,

$$S_{AB} = \int_{0}^{T} \frac{\gamma_{A} - \gamma_{B}}{T} dT$$
$$= \int_{0}^{T} \frac{\gamma_{A}}{T} dT - \int_{0}^{T} \frac{\gamma_{B}}{T} dT$$
$$= S_{A} - S_{B}$$
(23)

According to the third law of thermodynamics, the Seebeck coefficient is zero for all junctions at absolute zero temperature. Thus, the absolute Seebeck coefficient of any material is zero at this temperature.

From this, the absolute Seebeck coefficient of individual thermoelements can be found [14].

The absolute Seebeck coefficient of a material at very low temperatures may be determined by joining it to a superconductor. The latter possess a thermoelectric coefficient of zero while in the superconducting state (below the superconducting transition temperature). This procedure has been carried out for pure lead up to 18 K and the Thomson coefficient for lead has been measured between 20 K and room temperature. Its value in the range between 18 K and 20 K can be accurately extrapolated. Thus by using Equation 23, the absolute Seebeck coefficient of lead has been established. The absolute Seebeck coefficient of any other conductor may then be determined by joining it to lead. Lead is used because its absolute Seebeck coefficient is relatively small compare to other thermoelectric elements. Thus, when lead is used as a reference, the relative Seebeck coefficient of the thermocouple can be determined easily [13].


## 2.2 Theory of thermoelectric devices



Figure 2.5 Semiconductor based thermocouple.

One of the advantages of thermoelectric generation or refrigeration is the independence of the efficiency on the capacity of the unit. The coefficient of performance of a thermoelectric refrigerator can, therefore, be derived on the basis of the single thermocouple (Figure 2.5). It is assumed that the heat that flows from heat source to the heat sink is only through conduction through the branches of the thermocouple. The thermocouple is connected electrically in series and thermally in parallel. The number of the thermocouples being connected will affect the power handling capacity of the converter but not the efficiency.



Figure 2.6 Thermoelectric module.

If a voltage source is connected across the thermocouple to conduct a current flow, the thermocouple acts as a heat pump. For example, if a positive voltage source is applied to the thermocouple (Figure 2.6), current flows from p to n. In the p-type element, the majority carriers are holes. The holes flow from the lower plate to the upper plate carrying charge and heat as they flow. As the holes cross the junction to recombine with electrons in the upper metal contact, they dissipate heat. Likewise, heat is absorbed as holes enter at the lower contact. On the other hand, the electrons in the n-type element flow from the lower plate to the upper plate (in contrast to the current flow direction). Thus the electrons also flow from the bottom of the device to the top, also carrying charge and heat as they flow. As electrons enter the n-type semiconductor from the lower electrode they must absorb some energy (heat) to enter the conduction band of the semiconductor. As the electrons enter the upper metal electrode, they must release energy (heat) to enter the metal [18]. By reversing the current direction, the top metal electrode is cooled, while the bottom electrode is heated, thus acting as a heat pump. The total resistance *R* of the couple is,

$$R = \frac{l_p \rho_p}{A_p} + \frac{l_n \rho_n}{A_n} \tag{24}$$

The thermal conductance *K* of the two branches of the thermocouple in parallel is

$$K = \frac{A_p \kappa_p}{l_p} + \frac{A_n \kappa_n}{l_n}$$
(25)

where *l* is the length, *A* is the cross-section area,  $\rho$  is the electrical resistivity and  $\kappa$  is the thermal conductivity of an element. The ratio of  $l_p/A_p$  and  $l_n/A_n$  can be different from one another because the steady-state condition is unaffected by the shape of branches.

Peltier and Seebeck effects are bulk phenomena, i.e. they depend on bulk rather than surface properties of the materials. Thus, the external contact potential has no relationship whatsoever to any thermoelectric phenomena. When a current, *I*, flows through a conductor, it transports heat. As the current passes into another conductor, the heat transport is different. In the two branches of the thermocouple, the heat transport from the source to the sink is

$$q_{p} = S_{p}TI - \kappa_{p}A_{p}\frac{dT}{dx}$$
(26a)

$$q_n = -S_n T I - \kappa_n A_n \frac{dT}{dx}$$
(26b)

*T* is absolute temperature. Due to the Joule effect, the rate of heat generation per unit length in each branch is

$$-\kappa_p A_p \frac{d^2 T}{dx^2} = \frac{I^2 \rho_p}{A_p}$$
(27a)

$$-\kappa_n A_n \frac{d^2 T}{dx^2} = \frac{I^2 \rho_n}{A_n}$$
(27b)

By setting the boundary condition,  $T=T_1$  at x=0 and  $T=T_2$  at  $x=l_p$  or  $l_n$ , We find,

$$\kappa_{p}A_{p}\frac{dT}{dx} = -\frac{I^{2}\rho_{p}(x-l_{p}/2)}{A_{p}} + \frac{\kappa_{p}A_{p}(T_{2}-T_{1})}{l_{p}}$$
(28a)

$$\kappa_n A_n \frac{dT}{dx} = -\frac{I^2 \rho_n (x - l_n / 2)}{A_n} + \frac{\kappa_n A_n (T_2 - T_1)}{l_n}$$
(28b)

The combination of Equation26 and Equation 28 gives the rate of heat flow at x=0

$$q_{p}(x=0) = S_{p}TI - \frac{\kappa_{p}A_{p}(T_{2}-T_{1})}{l_{p}} - \frac{I^{2}\rho_{p}l_{p}}{2A_{p}}$$
(29a)

$$q_n(x=0) = -S_n T I - \frac{\kappa_n A_n (T_2 - T_1)}{l_n} - \frac{I^2 \rho_n l_n}{2A_n}$$
(29b)

Thus, the cooling power  $q_c$  at the heat source is  $q_c = q_p + q_n$ ,

$$q_{C} = (S_{p} - S_{n})T_{1}I - \frac{1}{2}I^{2}R - K(T_{2} - T_{1})$$
(30)

where half of the overall Joule heating goes to each junction. The cooling effect is opposed by Joule heating in the branches and by heat conducted from the hot junction.

The rate of electrical energy supplied, *W* in each branch is

$$W_{p} = S_{p}I(T_{2} - T_{1}) + \frac{I^{2}\rho_{p}l_{p}}{A_{p}}$$
(31a)

$$W_n = -S_n I(T_2 - T_1) + \frac{I^2 \rho_n l_n}{A_n}$$
(31b)

Part of the potential difference applied to the couple is employed in overcoming the resistance of the branches and part is used to balance the Seebeck voltage resulting from the temperature difference between the junctions. Thus, the power *W* supplied to the couple is given by

$$W = (S_p - S_n)I(T_2 - T_1) + I^2R$$
(32)

The coefficient of performance for refrigerator is defined as the ratio of  $q_C/W$ , which is the net heat absorbed/applied electric power,

$$\phi = \frac{q_C}{W} = \frac{(S_p - S_n)T_1I - \frac{1}{2}I^2R - K(T_2 - T_1)}{(S_p - S_n)I(T_2 - T_1) + I^2R}$$
(33)

## 2.3 Figure-of-Merit

In order to obtain a maximum cooling power, we take  $dq_C/dI = 0$  in Equation 30, to yield the current for maximum heat absorption

$$I_{q} = \frac{(S_{p} - S_{n})T_{1}}{R}$$
(34)



The maximum cooling power is then,

$$(q_C)_{\max} = \frac{(S_p - S_n)^2 T_1^2}{2R} - K(T_2 - T_1)$$
(35)

Equation 35 shows that if the temperature difference between the junctions is too large, maximum cooling power will not be achieved. By setting  $(q_c)_{max}=0$ , we can find  $(T_2-T_1)_{max}$ ,

$$(T_2 - T_1)_{\max} = \frac{(S_p - S_n)^2 T_1^2}{2KR}$$
(36)

The figure-of-merit of the thermocouple is

$$Z = \frac{(S_p - S_n)^2}{KR}$$
(37)

Equation 36 can be rewritten as

$$(T_2 - T_1)_{\max} = \frac{1}{2}ZT_1^2$$
(38)

For a given pair of thermoelectric materials, and for a given hot and cold junction temperatures, the coefficient of performance is a function of the current *I*, the resistance *R*, and the thermal conductance *K*. For a specified cooling capacity, the ratio of length to cross-section area for an element should rise with the electrical and thermal conductivities. A balance is then struck between the effects of resistance heating and thermal conductance. It shows that the coefficient of performance reaches a maximum value when the dimensions of the elements obey the rule

$$\frac{l_n A_p}{l_p A_n} = \left(\frac{\rho_p \kappa_n}{\rho_n \kappa_p}\right)^{1/2}$$
(39)

$$KR = \left\{ \left( \kappa_{p} \rho_{p} \right)^{1/2} + \left( \kappa_{n} \rho_{n} \right)^{1/2} \right\}^{2}$$
(40)

The figure of merit is

$$Z = \frac{(S_p - S_n)^2}{\left\{ \left( \kappa_p \rho_p \right)^{1/2} + \left( \kappa_n \rho_n \right)^{1/2} \right\}^2}$$
(41)

The figure of merit, *Z*, involves the mean values of all the parameters, Seebeck, electrical and thermal conductivities. It is most convenient to deal with the figure of merit for a single material as suggested by Equation 37. Thus, *Z* for a single material is

$$z = S^2 \frac{\sigma}{\kappa}$$
(42)

 $\sigma$  is electrical conductivity and it is equal to  $1/\rho$ .

In general, Z must be regarded as a rather complicated average of  $z_p$  and  $z_n$ . The use of an individual figure of merit as defined in Equation 39, is justified by the fact that nowadays the values of  $z_p$  and  $z_n$  are never very much different in the thermocouples which are most suitable for thermoelectric applications.

#### 2.4 The efficiency of a thermoelectric generator



Figure 2.7 Thermoelectric Power Generator.

In Figure 2.7, one junction of a thermocouple is connected to a source of heat while the other is in thermal contact with a heat sink. Power is delivered to a load of resistance  $R_L$ . The efficiency of the generator is defined as the ratio of the useful rate of working, *W* to the rate of heat supply, *Q* from the source. The heat supplied is either conducted along the branches to the cold junction or used to balance the Peltier effect at the hot junction. However, half of the Joule heating in the thermocouple finds its way back to the source. Thus,

$$Q = K(T_2 - T_1) + (S_p - S_n)T_1I - \frac{1}{2}I^2R$$
(43)

For maximum power output from a given couple the load resistance  $R_L$  should be made equal to the generator resistance R. The useful work is then,



$$W = \frac{(S_p - S_n)^2 (T_2 - T_1)^2}{4R}$$
(44)

Let  $\Delta T = (T_1 - T_2)/2$  and  $T_M = (T_1 + T_2)/2$ . Since  $IR_L = IR = (1/2)S_{np}\Delta T$ ,

$$Q = K(T_2 - T_1) + (S_p - S_n)^2 (T_M + \frac{\Delta T}{2}) \frac{\Delta T}{2R} - \frac{(S_p - S_n)^2 \Delta T^2}{8R}$$
(45)

i.e. half of the thermoelectric voltage appears across the load. The efficiency is

$$\varphi = \frac{W}{Q} = \frac{\Delta T}{2T_M + \frac{\Delta T}{2} + \frac{4RK}{(S_p - S_n)^2}}$$
(46)

The dimensions of the elements should obey Equation 39 giving

$$\varphi = \frac{\Delta T}{2T_M + \frac{\Delta T}{2} + \frac{4}{Z}}$$
(47)

Since the efficiency rises with Z this quantity is a figure of merit for thermoelectric generation as well as for refrigeration.

If *Z* tends to infinity  $\varphi$ , as given by Equation 47, approaches the value  $\Delta T/(2T_M + \Delta T/2)$  which is only half the efficiency of an ideal thermodynamic machine. The reason is that, when the maximum efficiency is required,  $R_L$  should not be made equal to R. It may be shown that the maximum efficiency is obtained when

$$r = (1 + ZT_M)^{1/2}$$
(48)

where r denotes the ratio  $R_L/R$ . Then

$$\varphi_{\max} = \frac{\Delta T}{\frac{(r+1)T_M}{r-1} + \frac{\Delta T}{2}}$$
(49)

Harman has shown that the efficiency of a thermoelectric generator may be improved by the use of a cascade arrangement. In his system the same current passes through the thermoelements; for each stage the number of couples and their dimensions are chosen so that conditions Equation 39 and Equation 48 are satisfied.

#### 2.5 Thermoelectric properties of semiconductors

The Wiedemann-Franz law states that the thermal to the electrical conductivity ratio is constant for all metals at a given temperature. Thus, when the Seebeck coefficient reaches its highest, the metal obtains maximum figure of merit. However, non-metallic thermocouple can give a higher differential Seebeck coefficient compared to metallic elements or compounds.

# 2.5.1 The thermoelectric coefficients of a non-degenerate semiconductor

In an insulator, the valence band is completely filled with electrons and the conduction band is completely empty of electrons. A forbidden energy gap, commonly known as band gap, separates the two bands. As the band gap of the insulator is large ( $\geq$ 3eV), the resistivity is too large for appreciable current flow, and the figure of merit, *Z*, is low. A semiconductor basically has the same band structure as the insulator, however, with a much smaller band gap ( $\leq$ 3eV) and this allow electrons

to be excited from the valence band to the conduction band by thermal generation. An ideal intrinsic semiconductor is a perfect crystal with no impurities or lattice defects and the charge carriers are only the electronhole pairs. As an example, gallium arsenide has a bandgap of 1.42 eV and an intrinsic carrier concentration of  $2.1 \times 10^6 \text{ cm}^{-3}$  at 300 K. When the semiconductor is doped with impurities (donors or acceptors), excitation of electrons from valence band to conduction band will occur even at relatively low temperatures. This is called an extrinsic semiconductor. Semiconductors are called *n*-type when the conduction of electricity is primarily due to electrons and *p*-type is due to holes [19].

It is important to introduce the Fermi level here. At absolute zero temperature, the energy states up to the Fermi level are filled with electrons and the higher states are empty. For a metal at some finite temperature, the states are partially filled over a range of energy within about 2kT of the Fermi level, where k is the Boltzmann's constant  $(8.616 \times 10^{-5} \text{ eV/K})$ . The probability of finding an electron in any given state is directly proportional to the energy difference between the corresponding state and the Fermi level.

A junction between an extrinsic semiconductor and an ideal metal will be considered here. The latter is defined as a metal in which it will be supposed that all the current carriers travel at the Fermi level of energy. The absolute thermoelectric coefficients of such a metal are zero. In real metals, the carriers occupy a small distribution of energies about the

Fermi level leading to finite, yet small thermopowers. In equilibrium, the Fermi level of the metal and semiconductor will align.

Suppose that the Fermi level of a metal is higher than a *n*-type semiconductor, then electrons will flow from the metal into the semiconductor. In order to rise into the conduction band of the latter it is necessary that an amount of potential energy - $\zeta$  should be absorbed for a single electron.  $\zeta$  is the Fermi potential and is positive when the Fermi level lies within the energy band and negative when it lies within the band gap. In carrying current through the semiconductor the electron travels with a certain kinetic energy  $\varepsilon$  which is measured from the band edge. It, therefore, absorbs an amount of energy ( $\varepsilon$ - $\zeta$ ) at the junction. This absorption of energy is the origin of the Peltier cooling effect at metal to semiconductor junctions, and the Peltier coefficient is, thus, the average value of this energy change per unit charge. By convention it is negative for an *n*-type semiconductor and it is then positive for a *p*-type material.

The potential energy of a non-degenerate semiconductor is greater than 2kT and the average kinetic energy of electrons in the conduction band is on the order of (3/2)kT. The average kinetic energy must account for the relaxation time due to scattering effects of charge carriers. The average kinetic energy also depends on the density of states since it varies with energy. Usually, the density of states is proportional to  $\varepsilon^{0.5}$ and the relaxation time for the charge carriers can be expressed as

$$au_e \propto \mathcal{E}^{\lambda}$$
 (50)

Where  $\lambda$  is constant. Then

$$\Pi_{n} = -\frac{1}{e} \left\{ \left( \frac{5}{2} + \lambda \right) kT - \zeta \right\}$$
(51)

Thus, the Kelvin's relations,

$$S = \frac{\Pi_n}{T} = \mp \frac{k}{e} \left( \frac{5}{2} + \lambda - \eta \right)$$
(52)

where the negative sign applies to *n*-type material, the positive sign to *p*-type material, and  $\eta$  is known as the reduced Fermi potential, equal to  $\zeta/kT$ .

If the carriers are scattered by the acoustical modes of vibration of a covalent lattice,  $\lambda$  is equal to -1/2. If the scattering mode is ionizedimpurities,  $\lambda$  is equal to 3/2. In many cases, these and other forms of scattering may be present so an approximation is used to express the relaxation time as a simple function of the energy.

#### 2.5.2 Electronic conduction in a non-degenerate semiconductor

For an *n*-type non-degenerate semiconductor, the Seebeck coefficient can be expressed in terms of the reduced Fermi potential and the electrical conductivity is

$$\sigma = n e \mu \tag{53}$$

Where *n* is the number of charge carriers per unit volume and  $\mu$  is the drift mobility of the carriers, defined as their average drift velocity in a

unit electric field. For a non-degenerate semiconductor the carrier concentration is given by

$$n = 2 \left(\frac{2\pi m * kT}{h^2}\right)^{3/2} \exp\eta$$
 (54)

Where *h* is Planck's constant and *m*<sup>\*</sup> is the effective mass of the carriers. By using this effective mass, rather than the free electron mass *m*, it is possible to treat the carriers as of they were free charges, in spite of the fact that they move in the periodic field of the crystal lattice. The carrier concentration given by Equation 54 corresponds to  $2(2\pi m^*kT/h^2)^{3/2}$ electron states located at the edge of the appropriate band though, of course, in reality the state are spread out over an effectively infinite range of energies. The quantity  $2(2\pi m^*kT/h^2)^{3/2}$  is known as the effective density of states.

Both the charge carriers and the lattice contribute to the conduction of heat through a semiconductor. Thus, the overall thermal conductivity is

$$\kappa = \kappa_{l} + \kappa_{e} \tag{55}$$

where  $\kappa_l$  is the lattice component of the thermal conductivity and will be considered in more detail later, and  $\kappa_e$  is the electronic component.

The amount of the heat that the charge carriers can conduct depends on their mean kinetic energy and this is according to their relative diffusion rates. It may be shown that, for a non-degenerate conductor, the weighting factor is exactly the same as that employed in

calculating the Peltier coefficient; the mean kinetic energy is  $(5/2 + \lambda)kT$ per unit charge. It is thus found that

$$\kappa_e = \left(\frac{5}{2} + \lambda\right) \left(\frac{k}{e}\right)^2 \sigma T \tag{56}$$

#### **2.5.3 Intrinsic Conduction**

At a sufficiently high temperature (or for low doping levels), the concentration of carriers can be dominated by thermally generated (or intrinsic) electron hole pairs. At these temperatures, the electron and hole concentrations are almost the same. Under these conditions, a mixed conduction will occur with both electrons and holes making significant contributions. The Seebeck coefficient can then be calculated by

$$S = \frac{S_n \sigma_n + S_p \sigma_p}{\sigma}$$
(57)

where  $\sigma_n$  and  $\sigma_p$  are the contributions to the electrical conductivity from the electrons and holes respectively, and  $\sigma_n$  and  $\sigma_p$  are calculated separately for electrons and holes using Equation 53 and the appropriate substitution of *p* for *n*.

The electrical conductivity of a mixed conductor is given by

$$\sigma = e(n_n \mu_n + n_p \mu_p) \tag{58}$$

where the electron and hole concentrations,  $n_n$  and  $n_p$  respectively are related by the mass action law

$$n_n n_p = 4 \left(\frac{2\pi m kT}{h^2}\right)^3 \left(\frac{m_n * m_{p^*}}{m^2}\right)^{3/2} \exp\left(-\frac{\varepsilon_g}{kT}\right)$$
(59)

Suppose that there is temperature-independent extrinsic carrier concentrations upon which are superimposed concentrations of intrinsically excited electrons and holes. For simplicity it will be assumed that the mobilities of electrons and holes are equal. Let the electron and hole concentrations in a region at temperature T be  $n_n$  and  $n_p$ respectively. Then for  $n_n$  electrons travelling to another region at a temperature T-dT there will be  $n_p$  holes, and thus, according to the normal electron theory, the kinetic energy transferred must be

$$[(\frac{5}{2} + \lambda)(n_n + n_p)\kappa\Delta T$$
(60)

However, because of the lower temperature of the second region, *dn* electrons must recombine with the same number of holes and each such combination liberates an amount of energy equal to the width of the forbidden band (assuming no photon emission occurs). Since the kinetic energy of the carriers is also transferred to the lattice the total heat transport is

$$\left[\left(\frac{5}{2} + \lambda\right)\left(n_n + n_p\right)k\Delta T + \Delta n\left\{\varepsilon_q + (5 + 2\lambda)kT\right\}\right]$$
(61)

Now from Equation 61, remembering that  $(n_n - n_p)$  must be independent of temperature,

$$\Delta n = \frac{n_n n_p}{n_n + n_p} \left( \frac{\varepsilon_g}{kT} + 3 \right) \frac{\Delta T}{T}$$
(62)

Thus, the ratio of the total electronic heat conductivity to the value in Equation 56 is

$$\frac{(\kappa_e)_{total}}{(\kappa_e)_{kinetic}} = 1 + \frac{n_n n_p}{(\frac{5}{2} + \lambda)(n_n + n_p)^2} \left(\frac{\varepsilon_g}{kT} + 3\right) \left(\frac{\varepsilon_g}{kT} + 5 + 2\lambda\right)$$
(63)

Taking into account the difference between the mobilities of electrons and holes and including thermal diffusion effects gives:

$$\kappa_{e} = \{ (\frac{5}{2} + \lambda_{n})n_{n}\mu_{n} + (\frac{5}{2} + \lambda_{p})n_{p}\mu_{p} \} \frac{k^{2}}{e}T + \frac{n_{n}\mu_{n}n_{p}\mu_{p}}{(n_{n}\mu_{n} + n_{p}\mu_{p})} \left( \frac{\varepsilon_{g}(0)}{kT} + 5 + \lambda_{n} + \lambda_{p} \right) \frac{k^{2}}{e}T$$
(64)

where Equation 64 is the energy gap extrapolated to 0 K.

It may be shown that, even in the intrinsic range, the value of the second term in the Equation 64 for InSb is less than the first term, which is the kinetic energy contribution. This is because the ratio of the electron mobility to the hole mobility is about 85. In bismuth telluride, however, the mobilities of electrons and holes are of the same order and it is found that, in an intrinsic material, the second term in Equation 64 is an order of magnitude larger than the first term.

## 2.5.4 Electronic properties of a degenerate conductor

There is a higher probability that any of the lower energy states will be filled when the reduced Fermi potential is greater than -2. Thus, Fermi-Dirac statistics must be used. For a highly degenerate conductor, that is when  $\eta$  is greater than 4, simple approximations to the Fermi-Dirac integrals may be used, but for thermoelectric applications, we are usually concerned with the intermediate range of partial degeneracy.

If the conductor is partially or completely degenerate, the concept of an effective density of states breaks down and the carrier concentration must be expressed as

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi m kT}{h^2}\right)^{3/2} F_{1/2}$$
 (65)

where

$$F_r = \int_0^\infty \xi^r f_0(\eta) d\xi$$
 (66)

 $\xi$  is the reduced kinetic energy of the carriers and is equal to  $\epsilon/kT$ . The Fermi distribution function is given by

$$f_0(\eta) = \frac{1}{1 + \exp(\xi - \eta)}$$
(67)

It is usual to express the electrical conductivity directly as

$$\sigma = \frac{16\sqrt{2}\pi m^{*1/2} e^2}{3h^3} \int_0^\infty \tau_e(\xi) \xi^{3/2} \frac{df_0}{d\xi} d\xi$$
(68)



but it is still possible to use Equation 53 provided that it is realized that the mobility is no longer independent of the Fermi potential, even in the absence of impurity scattering. In this case the mobility,  $\mu$  may be expressed in terms of the mobility  $\mu_0$  in non-degenerate material as

$$\mu = \frac{\sqrt{\pi}}{2\Gamma(\frac{3}{2} + \lambda)} \cdot \frac{F_{1/2+\lambda}}{F_{1/2}} \cdot \mu_0$$
(69)

The gamma function is defined as

$$\Gamma(y) = \int_{0}^{\infty} x^{y-1} \exp(-x) dx$$
(70)

When Fermi-Dirac statistics are applicable the Seebeck coefficient is given by

$$S = \frac{k}{e} \left\{ \frac{\left(\frac{5}{2} + \lambda\right)F_{3/2+\lambda}}{\left(\frac{3}{2} + \lambda\right)F_{1/2+\lambda}} - \eta \right\}$$
(71)

The electronic component of the thermal conductivity may be written as

$$\kappa_e = L\sigma T \tag{72}$$

where the Lorenz number *L* is given by

$$L = \frac{(\frac{3}{2} + \lambda)(\frac{7}{2} + \lambda)F_{1/2+\lambda}F_{5/2+\lambda} - (\frac{5}{2} + \lambda)^2 F^2_{3/2+\lambda}}{(\frac{3}{2} + \lambda)^2 F^2_{1/2+\lambda}} \left(\frac{k}{e}\right)^2$$
(73)

When the material is very strongly degenerate, Equations 65, 69, 71, 73 may all be simplified. The appropriate equations in this case are

$$n = \frac{8}{3\sqrt{\pi}} \left(\frac{2\pi m * kT}{h^2}\right)^{3/2} \eta^{3/2}$$
(74)



$$\mu = \frac{3\sqrt{\pi}\eta^{\lambda}}{4(\frac{3}{2} + \lambda)\Gamma(\frac{3}{2} + \lambda)^{\mu_0}}$$
(75)

$$\alpha = \mp \frac{\pi^2}{3} \cdot \frac{k}{e} \cdot \frac{\frac{3}{2} + \lambda}{\eta}$$
(76)

$$L = \frac{\pi^2}{3} \left(\frac{k}{e}\right)^2 \tag{77}$$

#### 2.5.5 Heat conduction by the lattice

It is shown that the thermal conductivity could be expressed as the sum of an electronic component  $\kappa_e$  and a lattice component  $\kappa_i$ . The lattice component,  $\kappa_i$ , represents the conduction of heat by the lattice vibrations of the crystal. In metals  $\kappa_i$  is usually negligible in comparison with  $\kappa_e$ , but it provides the sole contribution to the thermal conductivity of an electrical insulator and it is predominant in most semiconductors.

The thermal vibrations of the lattice may be quantized as phonons with a mean free path  $l_l$ . As was first shown by Debye, the thermal conductivity of a dielectric crystal may be expressed in the form

$$\kappa_l = \frac{1}{3} cvl_t \tag{78}$$

where *c* is the specific heat per unit volume and *v* the velocity of sound. If the vibrations are completely harmonic the value of  $l_t$  must be infinite for a perfect crystal. However, if the anharmonic nature of the vibrations is taken into account  $l_t$  becomes finite. In the region of the Deybe temperature and above, the phonons are primarily scattered by collisions



with other phonons. Their free path length is determined by the anharmonicity of the thermal vibrations and by their intensity. The intensity of the vibrations is proportional to the temperature so the phonon free path and, thus, the thermal conductivity of the lattice are inversely proportional to the temperature.

At very low temperatures boundary scattering of the phonons becomes predominant in a good crystal, so that the phonon free path depends only on the size of the sample. In this range the specific heat and the thermal conductivity are proportional to  $T^3$ . The thermal conductivity reaches a maximum value at a temperature approximately equal to one twentieth of the Debye temperature.

The value of  $\kappa_1$  in the region of the maximum may be limited by factors other than size of the specimen. Scattering of phonons by impurities or by lattice defects may be appreciable and, in some elements, the difference between the atomic weights of the isotopes has reduced the phonon free path. In an amorphous substance the free path length remains of the order of the interatomic spacing at all temperatures.

## 2.6 Optimization of carrier concentration

Since the Seebeck coefficient and electrical conductivity depend strongly on the Fermi level (which in turn depends upon the carrier concentration, the carrier effective mass, and the temperature), it is



convenient to express the thermoelectric transport coefficients in terms of the Fermi energy,  $E_F$  (conventionally measured from the band edges).



Figure 2.8 Variation of the figure of merit with carrier concentration.

On the other hand, thermal conductivity depends weakly on the carrier concentration and by increasing the carrier concentration, it will thus give a better figure of merit.

## 2.7 Material preparation

After the discovery of Seebeck and Peltier effects, many materials are identified to have interesting thermoelectric properties. In the beginning, metals and metal alloys were often used for temperature measurements.

In the late 1940s, interest in elemental semiconductors grew, and in the 1950s, compound semiconductors were heavily investigated. Among them, chemical compounds and solid solution gave the best and



most promising thermoelectric results. To obtain high thermoelectric efficiency, materials with high carrier concentrations are desired, however, materials with high doping levels tend to posses low carrier mobility, which can reduce the thermoelectric efficiency. To achieve a combination of high carrier concentration and perfect crystalline structure in a semiconductor is a very difficult task. This leads to developing better methods for 'modern' thermoelectric material preparation.

In order to facilitate characterization of a material, the material has to be as free of defects as possible. One way to achieve this goal is to grow single crystal or polycrystalline ingots with very large grains. Since the majority of modern thermoelectric materials are solid solutions or chemical compounds, it is important to understand the process of preparing these materials from a melt.

#### 2.7.1 Polychalcogenide flux method

The chemical reactions used in the polychalcogenide flux technique can be described as follows

 $M + xs - A_2Q_x \xrightarrow{\Delta} A_nM_yQ_m + A_2Q_m$  $MQ + xs - A_2Q_x \xrightarrow{\Delta} A_nM_yQ_m + A_2Q_m$ 

where

 $A_2Q_m$  is the solid solutions (chalcogenide compound)

Q is a chalcogen (S, Se, or Te)



M can be group IV or V: Pb, Bi, As

A can be from group I: Li, K, Cs

As examples consider the following reactions used in fabricating  $K_2Bi_8S_{13}$ , and the quaternary  $K_{1.25}Pb_{3.5}Bi_{7.25}Se_{15}$ 

e.g.  $K_2S + Bi_2S_3 \rightarrow KBi_{6.33}S_{10} + K_2Bi_8S_{13}$ 

 $2K_2Se + 2 \ Pb + 3Bi_2Se_3 + 10Se \rightarrow K_{1.25}Pb_{3.5}Bi_{7.25}Se_{15}$ 

One of the new material preparation techniques is the polychalcogenide flux technique designed by the Michigan State University Chemistry group. In Figure 2.9, a chalcogenide compound is vacuum-sealed in a test tube and heated either in flame or in the furnace. This allows for low temperature growth (200<T<600 C). Materials such as Bi2Te3 have traditionally been processed at temperatures >500 C. This growth technique, thus, allows for lower temperature growth of new crystal structures, previously unexplored. After reacting, the molten salt is cooled down at a rate of  $\sim 2C/hr$ . Excess  $A_2Q_x$  is washed away with water or some other polar solvent. The molten chalcogenide salt provides a medium in which reactants can dissolve thus accelarating the reaction. The molten salt also provides a medium for the product of the constituents to recrystallize thus promoting crystal growth. This method provides the ability to produce a pure form, more complicated compounds such as ternary or quaternary materials that would decompose at higher processing temperatures.





#### 2.7.2 Flash synthesis

After a certain type of chalcogenide compound has been produced from the flux method and shown to have promising thermoelectric properties, flash synthesis can be used to reproduce this type of compound in larger quantities. In the flash synthesis technique the correct element component ratios are used such that there are no excess reactants after the ingot is formed.

## 2.8 Sample Mounting Technique

The purpose of this system is to rapidly evaluate a large number of samples, through thermopower measurements, to gain insight on general doping and alloying trends. The most promising samples are then further characterized by measuring electrical conductivity, thermopower, and thermal conductivity in a 4-sample measurement system [12].


#### Chapter 3

## **Experimental set-up**

# **3.1 Apparatus**

A system that can measure the thermoelectric power of up to 36 samples simultaneously, is presented. The whole system consists of a Measurement Unit, a Janis Supertran Unit (sub-system), a Vacuum Unit (sub-system) and a Software Unit, Figure 3.1. The following are the detailed description for each component in each unit:

#### **3.1.1 Measurement Unit**

## 3.1.1.1 Keithley 7002 High Density Switch System

The Model 7002 Switch System is a 10-slot mainframe that supports up to 400 2-pole multiplexer channels or 400 matrix crosspoints. This is a computer controlled relay bank to connect the appropriate meter(s) to the desired sample(s). The front panel includes a unique interactive display of channel status for quick programming. Scanning speeds of up to 165 channels per second are possible with the high-density switch cards.

It has nine 20-channel relay switch card slots of which two are being used in this system. The system is connected to the sample cryostat, the source meter, six Nanovoltmeters and a Lock-in Amplifier. By closing the appropriate relays in the 7002, corresponding samples are selected for measurement.





## 3.1.1.2 Keithley 2400 Digital Source Meter

This meter consists of four instruments in one: a voltage source, a voltage meter, a current source and current meter. It can source up to 20 watts, allows sourcing and measuring of voltage from +/-1 uV to +/-200 VDC and current from +/-10pA to +/-1A. It can also automatically generate sweeps of output voltage or current vs. time.

On board memory of this meter can be used to store measured data for review or for block transfer to a computer. In this system, it is used to source current in the 36 sample measurement system

## 3.1.1.3 Keithley 2182 Nanovoltmeter

This meter is capable of 10nV resolution, and averaging multiple readings for noise reduction. In the 36 sample system, two 2182 meters are used to measure one sample at a time. One meter measures the voltage difference (dV), while the other simultaneously measures the temperature difference (dT). Temperature difference (dT) is measured using a copper constantan differential thermocouple. The voltage measured across the differential thermocouple is converted to a differential temperature reading using a reference thermocouple lookup table [20].



#### 3.1.1.4 LakeShore 330 Autotuning Temperature Controller

The system is capable of 4.2K to 400K operation and is temperature controlled using the LakeShore 330 Temperature Controller. This instrument compares the measured control sensor value to the desired control set point and minimizes the difference using the standard Proportional, Integral, Derivative (PID) control. Two heaters setting provide 25W and 50W maximum and accommodate a variety of cryogenic systems.

An autotuning algorithm is available, which determines controller gain (Proportional), reset (Integral), and rate (Derivative) by observing system time response upon setpoint changes under either P, PI or PID control.

Limitations to digital control and Autotuning:

 Any control system is inherently unstable if the sampling rate (frequency) is not greater than twice the system bandwidth (inverse of system time constant). Known as the Nyquist criterion
Autotuning requires system time response measured as a result of a change in temperature setpoint. Several points on this response curve must be measured to determine PID parameters.

LakeShore simplified the input of the rate time constant to correspond to a percentage of the reset time constant, i.e., 0 to 200%. So in manual mode with RATE set to 100%, any change in RESET causes

the controller to automatically calculate the RESET time constant and set the RATE time constant at 1/8 of the RESET time constant.

# 3.1.1.5 EG&G 7265 DSP (Digital Signal Processor) Lock-in Amplifier

This instrument has dual capability:

- 1. It can recover signals in the presence of an overwhelming noise background;
- 2. It can provide high-resolution measurements of relatively clean signals over several orders of magnitude and frequency.

It can function as: AC signal recovery instrument, vector voltmeter,

phase meter, spectrum analyzer, transient recorder, precision oscillator,

frequency meter and noise measurement unit. Its signal recovery mode is

the default mode on power-up. Its signal channel input can be used for

either single-ended or differential voltage mode operation, or single-ended

current mode operation.

In voltage mode, AC and DC coupling is available, also the input may be switched between FET and bipolar devices. In current mode, two conversion gains are available. In both modes, the input connector shells may be either floated via 1k ohm resistor or grounded.

#### **3.1.2 Janis Supertran Unit**

## **3.1.2.1 Cold Finger Cryostat**

This is the part of the system that interfaces with samples. It includes a copper cold finger with tapped mounting holes, heater and thermometer for monitoring and regulating the temperature. The system



is designed to operate with either liquid nitrogen or liquid helium as the working cryogen. As part of this thesis, this sample stage was designed and submitted to the Physics Machine Shop for fabrication. It was subsequently gold plated for surface stability.

## 3.1.2.2 High efficiency transfer line

The Janis Supertran transfer line combines vacuum insulation with multilayer superinsulation to provide low cryogen losses during transfer. A needle valve flow regulator is built-in to the transfer line. One end of the transfer line is inserted into the cryogen storage container (we use a liquid nitrogen tank here), while the other end is inserted into the cold finger cryostat.

## **3.1.2.3 Radiation shield**

This shield, usually fabricated from polished aluminum tubing, is mounted to a thermal anchor on the cold finger cryostat. It intercepts room temperature radiation, thereby reducing the heat load on the sample. This helps the system achieve lower sample temperatures and minimizes temperature gradients.

## 3.1.2.4 Liquid Nitrogen

The liquid nitrogen cools the samples and provides a temperaturecontrolled environment for obtaining temperature dependent



measurements. There is a temperature sensor (silicon diode) in the base of the cryostat that connects to the LakeShore 330 temperature controller. The sensor provides accurate temperature measurements (< 10mK accuracy) and feedback control to the temperature controller. Typical measurement runs are from 77K to 400K. The cryostat is also capable of liquid helium use for 4.2K to 400K operation.

## **3.1.3 Vacuum Unit**

The system needs to have a vacuum environment to prevent icing and heat loss through convection.

## 3.1.3.1 TURBO-V 70

Turbo-molecular pump has KF 40 NW high vacuum flange for high and ultra-high vacuum. The pumping action is obtained through a high speed turbine (max. 75000 rpm) driven by 3-phase electric motor.

# 3.1.3.2 TURBO-V 70 CONTROLLER

The controller drives the Turbo-V 70 pump during the starting phase by controlling the voltage and current with respect to the speed reached by the pump. The controller is a solid-state frequency converter that is driven by a single chip microcomputer and is composed of:

\* Power transformer

\* Front panel display and keyboard

- \* Rear panel with input/output connectors
- \* PCB including: power supply and 3-phase output, analog and input/output section, microprocessor and digital section, display and keyboard circuits.

The power supply converts the single-phase (50-60 Hz) AC mains supply into a 3-phase, low voltage, medium frequency output which is required to power the Turbo-V pump. The microcomputer generates the variable output frequency and controls the 3-phase output voltage according to the on board software and the gas load condition of the pump. It manages signals from sensors, input/output connection information to be displayed, and gives outputs for a fully automatic operation. A non-volatile RAM is used to store pump operating parameters.

The vaccum station is turned on by pressing the "Start" key of the controller. The controller starts the rough pump followed by the turbo pump automatically. The vacuum level can be monitored with the multigauge controller described below.

#### 3.1.3.3 Kurt J. Lesker Multi-Gauge Controller

It is used to control and read the pressure of the sample chamber. Plug-in Boards: 1) T/C gauge, 2) Bayard-Alpert and 3) RS232 Control and output. The thermocouple gauge board can monitor up to four thermocouple gauges. These gauges are capable of measuring from atmospheric pressure down to  $1.0 \times 10^{-3}$  Torr. Below this pressure, a



Bayard-Alpert ion gauge is used. This ion gauge has a tungsten filament and can measure pressures in the 10<sup>-4</sup> to 10<sup>-9</sup> Torr range. The ion gauge should always be turned off before removing the cryostat to avoid burning out the filament and contaminating the gauge.

## 3.1.4 Software Unit

A very significant feature of this system is the computer-control. By connecting GPIB cables to each instrument, it provides channels for communicating between the computer and the instruments. A graphical programming language was used for system control and data acquisition and was developed in LabVIEW<sup>®</sup>.

## 3.1.4.1 LabVIEW (Virtual Instrument) Programming

LabVIEW is a program development environment, much like modern C or BASIC development environments, and National Instruments LabWindows/CVI. However, LabVIEW is different from those applications in one important respect. Other programming systems use text-based commands to create lines of codes, while LabVIEW uses a graphical programming language, G, to create programs in block diagram form. A graphical icon within the program represents a subroutine, and data is passed in an out of these subroutines by connecting graphical wires between icons. LabVIEW is a general-purpose programming system, but it includes libraries for data acquisition, GPIB and serial

instrument control, data analysis, data presentation and data storage. LabVIEW programs are called virtual instruments (VIs) because their appearance and operation can imitate actual instruments. Figure 3.2 is the flowchart of the system's programming.

# 3.2 Design of the sample stages

The following set of figures show the details of this system, including drawings used in fabricating various parts of the sample stage.





Figure 3.2 Flowchart of the programming



Figure 3.3.1 and 3.3.2 show the top view of the circuit boards and sample stages of this system.

Figure 3.3.1(a) A 1.7" diameter circuit board with 76 holes (each hole is 0.035" diameter) distributed into four groups. Each hole has been soldered to a 0.4" length gold plated electrical pin. The four larger holes are the bolt positions.

Figure 3.3.1(b) A 1.7" diameter circuit board with 76 smaller holes (each hole is 0.067" diameter) and each hole will be soldered to a socket.

Figure 3.3.1(c) A 1.5" diameter circuit board with two rings of 36 holes each. It is placed under the 36-arm-spring for support purposes and each spring arm is soldered to the circuit board.

Figure 3.3.1(d) Support stage to hold the 36 springs to the proper. It is slightly larger than the pin and socket circuit boards. It will combine with the circuit board #b.

Figure 3.3.2(e) is a spring with 36 arms. The springs were originally connected by a ring of metal at the center of the spring assembly. This provided proper alignment while mounting the springs to a circuit board. After mounting, the inner metal ring was removed in order to produce 36 individual arms. The spring arm provides a flexible capacity to hold the sample in place during the measurement and accommodates samples of varying sizes.

Figure 3.3.2 (f) Stage that is bolted on the cryostat cold head.



Figure 3.3.2 (g) Sample holder stage with 36 dimples to hold each sample in place.

Figure 3.3.2 (h) Radiation shield.

Figure 3.4.1 and 3.4.2 show the brief process of how the whole sample stage is assembled.

In Figure 3.4.1(a, b), one side of the pin-circuit-board is soldered with 76 quad-twisted wires which are connected to the cryostat. The other side of the board is where the pins make contact (plug-in) with the 76 sockets. The quad-twisted wires are fed through the 4 holes of the sample stage #f. Sample stage #f is bolted to the cold head of the cryostat. These wires are soldered to the pins of 3 connectors inside the cryostat.

In Figure 3.4.1(c) and 3.4.2(d), the circuit board #b is combined with the support stage #d. The wiring of this circuit board will be explained later. The sample holder stage #g is placed on the stage #f and the combined stage #b and #d are placed on the top of the stage #g.

In Figure 3.4.2(e), part of the stage is assembled.

In Figure 3.4.2(f), solder was forced through the holes of the spring to make a robust contact with the circuit board #c. Part #c and #e are bolted to the top of the stage #d. Figure 3.5 is the top and side view of the stages after all parts are assembled.















Figure 3.4.2 The process of assembling the sample stages II





Tab to accommodate the common end of a differential thermocouple.

Top view of sample stage showing 36 samples near the perimeter, and 76 electrical pins closer to the center.



Figure 3.5 Stage with all parts assembled. The top and side view.

#### 3.3 Preparation for wiring of the sample stage

Two types of lead were used to measure the thermopower of each sample: the temperature leads (thermocouples) and the voltage leads.

$$S = dV/dT$$

A 1 K temperature drop is created across the sample using a surface mount resistor as a heater on each of the 36 springs.

1) Temperature lead (Thermocouples)

36 lengths of 5cm (0.003" diameter, Teflon insulated) copper and constantan wires were prepared. Both ends of each wire were scraped to remove the insulation and 36 pairs of copper-constantan thermocouples were made by spark welding the wires together.

2) Voltage lead

36 lengths of 5cm (0.003" diameter, Teflon insulated) copper wires were prepared. Both ends were scraped to remove the insulation

3) Heater

36 surface mount resistors were used as heaters to create the temperature gradient,  $\Delta T$ , across each sample. These  $\Delta T$  heaters were mounted near the end of each spring arm. Two copper wires (0.003" diameter, Teflon insulated) were soldered on each resistor, as shown in Figure 3.6(a).





Figure 3.6 Heater

(C)

 $470 \text{ x} 9 \Omega$ 

 $470 \ge 9 \Omega$ 



The temperature gradient should be created across the sample, while one end of the sample remains at the sample stage temperature. To avoid changes in the sample stage temperature, only half of  $\Delta T$  heaters (every other one) are heated at one time. Each of these two clusters consists of 18 resistors formed by the parallel connection of two groups of 9 series connected resistors. Figure 3.6(b) shows how two resistors are connected and Figure 3.6(c) shows the series combination of nine resistors per group. The two clusters share a common ground, however current is selected to pass through only one cluster at a time. Each surface mount resistor is 470  $\Omega$ , thus, the resistance per cluster is

R = 9\*470/2 = 2115 ohms

If current, I = 7 mA is supplied we get,

 $V = I^*R \approx 14.8 V$ 

By doing this simple calculation, we can set the limit on the voltage across these clusters. With this  $\Delta T$  heater configuration (two clusters of two groups each) the widest range of power from the current source is available.

# 3.3 Wiring the sample stage

With so many sample positions, it was essential to organize the wiring into smaller tasks. The following eight steps were used in wiring the sample stage.

Step 1: Mounting the  $\Delta T$  heaters on springs, Figure 3.6(d).

The  $\Delta T$  heaters were mounted on the spring in the following layered order Spring > Stycast epoxy > paper > Stycast epoxy > resistor > Stycast epoxy Stycast epoxy gives good thermal conduction but poor electrical conduction. It, thus, allows the heat from the resistor to conduct to the sample while preventing electrical shorting of the resistor through the spring. Paper was used to assure a physical separation between the  $\Delta T$ resistors and the spring was maintained while the epoxy dried. Kapton tape is used to tape down the wires on the spring to make the wires more stable in position and provide some strain relief for the wires.

Step2: All voltage and temperature leads (wires) were each soldered to the appropriate socket on the circuit board. 36 copper wires (for dV) and 36 copper wires (from copper-constantan thermocouple) were soldered to the sockets.

*Step3*: All wires were fed through the stage#d. This was very challenging as many wires were broken during this step. To help, groups of wires were twist-tied together and then slowly fed through each hole (in the stage Figure 3.3.1(d)).

Step4: Sparking the Constantan wire of the Thermocouples.

To reduce the number of wires traveling up the cryostat, the differential thermocouples were fabricated using one common junction thermally connected to the sample stage. This was assembled in the following manner: After all wires were fed through the stage, the ends of each constantan wire were sparked together in a single bundle. However, it is

pretty hard to make a big joint out of 36 wires, so smaller groups were sparked together electrically joined using constantan wires. A single constantan wire was then connected to this large bundle and used to form the common junction by spark welding it to a copper wire. All  $\Delta T$ measurements were made by measuring the voltage between this common copper wire and one of the 36 copper wires from the thermocouple attached to the end of a spring (as described in Step 2).

To further describe the sparking process: 1) A few constantan wires were twisted together; 2) A small constantan foil was folded over the twisted wires, leaving the ends sticking out of the foil; 3) The end wires were sparked causing them to melt back to the foil and form a strong joint. All of these small joints were wrapped with Kapton tape to prevent electrical shorts to the copper stage. They were further hidden between the support stage and the spring circuit board to protect them from mechanical disturbances.

*Step5*: Bolt down the spring to the support stage with a Teflon sheet in between.

*Step6*: With all the wires sticking out, start to tape down each thermocouple and voltage lead to their corresponding spring. This is an important part because wrong wiring will result in testing the wrong sample.




Step7: Mount the thermocouple on very end of each spring arm.

Thermocouple is mounted in the following order

Spring > Stycast epoxy > paper > Stycast epoxy > Thermocouple > Stycast epoxy

Step8: Mount the voltage leads.

Voltage leads will be soldered on each spring arm. Figure 3.7 shows the wiring on one sample.

#### 3.4 Preparation for the measurement: Testing

For this section, several figures are included to give a better view of how the wiring and testing work. Figure 3.8 - 3.11 show the wiring of different connectors which are plugged into the cryostat. Figure 3.12 – 3.15 show the wiring on four switch cards that are inserted to the 7002 switch system. Figure 3.16 shows the interconnection between the switch cards and other instruments.

*Step1*: A multimeter was used to test continuity between the leads at the instruments and the pins at the sample stage, to make sure there were no electrical shorts to the ground.

*Step2*: The voltage contacts were tested by checking continuity between the individual sockets and the corresponding spring contact.

*Step3*: The thermocouples could not be checked with the same methods used for the voltage leads because all thermocouples are jointed to a common point. Instead the thermocouples were checked by measuring

the resistance of each differential thermocouple. The resistance of all the thermocouple leads was found to be similar.

*Step4*: After testing the wiring on the spring and socket, it was plugged in to the stage. Care was taken to match each group of sockets to the corresponding pin-group.

*Step5*: Continuity was then tested between each spring contact and the cryostat's connector pins.

*Step6*: The 4 cable connectors (including the connector from the temperature controller) were then plugged into the cryostat. Further testing the connection between the meters and the stage.

Step7: All 2182 nanovoltmeters were then turned on and monitored as the appropriate relay closures in 7002 were made. With no temperature gradient, the  $\Delta T$  readings where found to be on the order of 0.001mV. Step8: The voltage leads were tested by closing the appropriate contacts in the 7002 switching system, unplugging the 2182 connectors and testing continuity between the 2182 connector pins and the corresponding spring. The continuity was monitored as the relay in the 7002 switching system was opened. With the relay closed, continuity between the 2182 connector and ground was also tested (to verify an open circuit condition with no sample present).

*Step9*: Finally the differential thermocouples were also tested by closing the appropriate contacts in the 7002 and monitoring the voltage from the corresponding differential thermocouple while gently warming the spring

(by placing a finger on it). The  $\Delta T$  voltages were observed to rapidly increase while touching the spring, and subsequently decrease upon removing the finger.

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# Inside view of the 10 pin connector



Outside view of the 10 pin connector





Figure 3.8 The inside and outside views of a 10 pin connector. It connects the temperature controller to the cryostat, reads and controls the temperature sensor which is mounted in the base of the cryostat.



Inside view of the 20 holes connector



Outside view of the 20 hole connector



C - B19 (Short to heater low,

common point for two groups of heaters)

- L C19 (heater reisistor)
- J D19 (heater reisistor)
- N C15
- S D9
- Q A19 (Short to six 2182 meters' ground,

physically ground to sample stage)

Figure 3.9 Inside and outside views of a 20 pin connector. It provides connection to the heater and extra pins to the cryostat.



Inside view of the 35 hole connector



Outside view of the 35 hole connector



Color of the wire Letter on the connector blk - black blu - blue brow- brown gr - green org - orange red - red whi - white ye - yellow

Figure 3.10 Wiring on 35 pin connector#1. It connects samples' lead to the switch system and meters.



Inside view of the 35 hole connector



Outside view of the 35 hole connector



Color of the wire Letter on the connector blk - black blu - blue brow- brown gr - green org - orange red - red whi - white ye - yellow

Figure 3.11 Wiring on 35 pin connector#2. It connects samples' lead to the switch system and meters.













Figure 3.14 Wiring on switch card #2a to the connectors.







Figure 3.16 Wiring of the four 20-channel relay switch card slots It also shows the connections to the 2400 source meter, 2182 voltmeters and lock-in amplifier

## **3.5 Load samples**

Samples dimensions from 3x3x7mm to 4x4x9mm can be accommodated in this system. Samples received with dimensions larger than these were cut into smaller pieces by using a diamond saw. Samples are easily mounted by slowly lifting the spring arm with a pair of tweezers while placing the sample under the spring. The spring arm thus holds the sample in place. Silver or gold paste can then be used for improved electrical and thermal contact to the spring and sample stage.

### 3.6 Test run

Reference materials of bismuth telluride  $Bi_2Te_3$ , and lead bismuth selenide Pb/Bi/Se, were first measured. These samples were received from industrial collaborators, and have been characterized in independent systems. While at room temperature, the source current from the 2400 meter was adjusted to create a temperature drop of ~1 K across the samples.

The samples were then prepared for temperature dependent measurements by loading them into the cryostat vacuum chamber. The bolts were then tightened and all electrical connectors plugged into the cryostat before turning on the vacuum pump. The cryogenic transfer line was then inserted into the cryostat. After releasing all pressure on the liquid nitrogen storage tank, the other end of the transfer line was inserted approximately 8 inches into the dewer (not far enough to touch



the liquid nitrogen). The valve on the transfer line was then opened to allow dry nitrogen gas to purge the transfer line of any moisture that might be in the line. This is an essential step to assure that ice does not form in the transfer line and clog it. Typically the first two or three data points are monitored to adjust the cryogen flow through the transfer line, however, since the system is computer-controlled, by entering the desired parameters, e.g. the temperature range, the pulse height, the period and etc, it can operate independently until the run is over.



## Chapter 4

## **Results and Discussion**

Each thermopower data point (at a given temperature) is obtained by fitting (linear) over 600 points of dV vs. dT data as shown in Figure 4.1. The two complete loops that fall on top of one another in this figure correspond to two periods of current through the  $\Delta T$  heater resistor for this sample.



Figure 4.1 dV/dT plot of sample#15 (Pb/Bi/Se) for 2.2 periods of the current pulse.

Figure 4.1 shows the dV/dT plotting for Pb/Bi/Se. The thermopower of the sample is the slope of dV/dT. Since the slope is negative, the thermopower is negative and thus the sample is *n*-type. For the indicated temperature gradient of approximately 1.35 K, the sample

voltage of nearly 50  $\mu$ V was measured, giving a thermopower of approximately -37  $\mu$ V/K at this temperature.



Figure 4.2 dV/dT plot of sample#1 (Bi<sub>2</sub>Te<sub>3</sub>) for 2.2 periods.

Similar measurements on *n*-type  $Bi_2Te_3$  are shown in Figure 4.2. In this case, the slope of the data indicate a thermopower of approximately -217  $\mu$ V/K in excellent agreement with measurements from independent systems.

The looping observed in Figures 4.1, and 4.2 occurs due to a temperature difference between the location of the thermocouple and voltage leads. While the thermocouple and voltage leads have been placed as closely together as possible, there is some separation across which small gradients could exist. As this system is used for screening

many samples, an accuracy of  $\pm 20\%$  is adequate and such small looping is acceptable. In comparison, Figure 4.2 has a much smaller looping indicating the sample dependence of this effect. Often the looping problem can be corrected by increasing the pulsing period. This is because the longer the period, the closer the system will come to reaching steady-state.



Figure 4.3 Two runs of sample#15 (Pb/Bi/Se) near room temperature.

The repeatability of thermopower measurements was investigated as shown in Figures 4.3, 4.4, and 4.5. Figure 4.3 shows repeatability within 1.25%. Figure 4.4 indicates repeatability of better than 0.2%, and Figure 4.5 shows approximately 1.7% repeatability.





Figure 4.4 Two runs of sample#26 (Bi<sub>2</sub>Te<sub>3</sub>) at room temperature.



Figure 4.5 Two runs of sample#32 (Bi<sub>2</sub>Te<sub>3</sub>) at room temperature.

Figures 4.3-4.5 show higher thermopower in the second run. This might due to unstable vacuum. After replacing the rubber O-ring with a copper plate for better sealing, the results are more consistent. This can be seen in Figures 4.6-4.9.

Figures 4.6-4.9 show the results of the first and second runs of 19 samples. Among them are 15 samples of bismuth telluride and 4 samples of lead bismuth selenide. The first and second runs gave very consistent results. The standard value of thermopower for  $Bi_2Te_3$  at room temperature is about -220  $\mu$ V/K. It is obvious that some of the samples did not give the correct thermopower values. Further explanation will be discussed. The results for lead bismuth sellenide have more deviation.



Figure 4.6 First run of 15 samples (Bi<sub>2</sub>Te<sub>3</sub>) at room temperature range.



Figure 4.7 Second run of 15 samples ( $Bi_2Te_3$ ) at room temperature range.



Figure 4.8 First run of 4 samples (Pb/Bi/Se) at room temperature range.



Figure 4.9 Second run of 4 samples (Pb/Bi/Se) at room temperature.



Figure 4.10 Comparison between this system's data (140K-300K) and data measured in an independent system.





Figure 4.11 Comparison between this system's data and standard Tellurex data (110K-300K)

Figure 4.10 and 4.11 are the plots including the reference data for these samples. In Figure 4.10, except #32, the other samples show good agreement with the reference data. All samples shown above indicate *n*type behavior. This system has also been utilized in characterizing *p*-type samples giving dV/dT plots similar to Figures 4.1 and 4.2, but with positive slopes.

Improper linear fitting in the software is suspected to have caused some bad data points as shown in Figure 4.11. Low temperature dV/dTplots have also shown increased noise potentially due to thermal contractions of the spring contacts and resulting degradation of the interface between sample and spring contact.

Images in this thesis are presented in color.


# **Chapter 5**

### **Further Improvement**

The system was designed to characterize 36 samples simultaneously but during the building process, many of the sample locations had problems caused by broken wires, bad thermocouples, or shorting to ground. The remaining positions have shown good results. The experience of building this system has been invaluable, particularly for identifying areas for further improvements including:

- Type of wires The wires that are used for voltage leads and thermocouples are formvar insulated and they are not suitable for high temperature measurement. Polyimide insulated wires can be considered since they can operate at a relatively high temperature, about 220C (473K). Gold wire was used in the original design for voltage but it was replaced by copper wire due to its brittleness. Though, gold wire will have low loss in electrical conduction. A redesign of the sample stage may be possible to better handle this fragile gold wire.
- 2) Wiring on stage As shown in the wiring figures, wiring all 36 thermocouples, 36 voltage leads and 36 surface mount resistors on a stage which is less than 2" diameter is not an easy job. Since all the wires are exposed, it is very easy to break the wires during the wiring process or even when loading the samples. Thus, a stage

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with hidden wires, such as in flexible circuit boards, will be one of our considerations in building the next stage.

- 3) Thermocouple thermocouples, which are used in this system are sparked welded. The joint of each thermocouple may be different and thus posses different resistance. Thermocouple junction quality is suspected as a reason for the deviation among samples of the same material. For our next revision, we might purchase pre-fabricated thermocouples.
- 4) Labview programming communication between computer and system did not always go smoothly. Since the system consists of 10 instruments, a slight delay on one of the meters might cause the whole system to lock up. Thus, improved communications and error handling would help to provide smooth measurement runs.
- 5) 2-probe electrical conductivity The system is also designed to add in more features in the future. 2-probe electrical conductivity measurements will be included in the run to better evaluate the sample quality.

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# Chapter 6

### Conclusion

A high sample throughput computer-control measurement system has been presented for characterizing the thermoelectric power of up to 36 samples in a single temperature run (4.2K – 400K). This will greatly increase the number of samples being characterized and thus speed up the exploration in the field of thermoelectrics.

Many significant features of the system, including computercontrol, easy sample mounting, and high sample throughput have made it a unique system for characterizing thermoelectric materials. We are not aware of anyone in the nation with such a capability. For comparison, a separate system in the same laboratory has been configured to measure up to 4 samples in a single run. The system described in this thesis can accommodate more than 5 times this number of samples. When investigating new thermoelectric materials, the use of this system can provide a broad perspective of sample variations with doping and alloying. It is, therefore, a good starting point in searching for new samples before proceeding with more exhaustive characterization techniques.



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