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COMPARISON BETWEEN STEADY STATE AND LASER FLASH TECHNIQUES

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COMPARISON BETWEEN STEADY STATE AND LASER FLASH TECHNIQUES

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Physics

by
Justine Elizabeth Andrews
August 2007

Accepted by:
Dr. Terry M. Tritt, Committee Chair
Dr. Apparo M. Rao
Dr. Catalina Marinescu

ABSTRACT

Thermoelectrics is a promising avenue of energy conservation. A material is deemed a good thermoelectric material when it portrays certain material characteristics. These characteristics include a high thermopower and electrical conductivity and a low thermal conductivity. This thesis focuses on the methods of measuring a material's thermal conductivity.

The steady state method is a measurement technique used in the low temperature thermal conductivity measurements. This technique assures that the system and sample are at equilibrium before a measurement point is taken. As a result the measurements are both precise and accurate.

The laser flash technique measures a sample's thermal conductivity to higher temperatures than the low temperature thermal conductivity system. This technique sends a laser into the sample and measures the heat flow through the sample using a detector located at the opposite end of the sample.

In this thesis each thermal conductivity measurement technique is explained in detail. Certain data is presented and explained from each system. Lastly both the data and systems are compared. As a result the reader will be prepared to mount and run samples as well as analyze data from each of the thermal conductivity systems.

ACKNOWLEDGMENTS

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TABLE OF CONTENTS

	Page
TITLE PAGE.....	i
ABSTRACT.....	iii
ACKNOWLEDGEMENTS.....	v
LIST OF FIGURES.....	x
 CHAPTER	
1. INTRODUCTION.....	1
2. LOW TEMPERATURE THERMAL CONDUCTIVITY	9
Experimental Procedure	9
Background.....	9
Experimental Apparatus	12
Sample Mounting.....	15
Experimental Results.....	19
3. LASER FLASH AND DSC	30
Laser Flash.....	30
Experimental Procedure	30
Background	30
Experimental Apparatus	30
Sample Mounting.....	37
Experimental Results.....	38
Differential Scanning Calorimeter.....	50
Experimental Procedure	50
Background	50
Experimental Apparatus	51
Sample Mounting.....	54
Experimental Results.....	54
4. COMPARISON	61

Table of Contents (Continued)

	Page
APPENDICES	64
A: Procedure List for mounting Low Temperature Thermal Conductivity Measurements.....	64
B: Procedure List for Preparing Laser Flash Thermal Diffusivity Measurements	65
C: Procedure List for Preparing DSC Measurements	66
D: Flow Chart for Running Low Temperature Thermal Conductivity System.....	67
E: Flow Chart for Running Laser Flash System.....	68
F: Flow Chart for Running DSC.....	69
G: Advantages and Disadvantages of the Low Temperature Thermal Conductivity System.....	71
H: Advantages and Disadvantages of the Laser Flash System.....	72
I: List of Considerations Before Running a Sample.....	73
REFERENCES	74

LIST OF FIGURES

Figure	Page
1. Thermoelectric Modules	3
2. State of the Art Thermoelectric Materials	6
3. Power vs. Delta T Sweep	11
4. Thermal Conductivity System	13
5. Sample mounted with thermocouple and heater wires attached	14
6. Low Temperature Thermal Conductivity Mount.....	17
7. Sample Mounted for Low Temperature Thermal Conductivity Runs	18
8. Resistivity vs. Temperature of HfZrNiSnSb.....	21
9. Smooth fit Electrical Conductivity vs. Temperature of HfZrNiSnSb	22
10. Comparison of total, electrical, and lattice thermal conductivities in HfZrNiSnSb	23
11. Lattice Thermal Conductivity Comparison between $ZrNiSn_{0.975}Sb_{0.025}$ and $Hf_{0.75}Zr_{0.25}NiSn_{0.975}Sb_{0.025}$	25
12. Radiation tail present in Bi_2Te_3	27
13. Linearity of the change in lattice thermal conductivity vs. temperature ³	28
14. Laser Flash diagram	33
15. Netzsch LFA 457 MicroFlash®	34
16. Half-time Method	35
17. Half-time of ZrNiSnSb sample measurement	36

List of Figures (Continued)

Figure	Page
18. Reproducibility of thermal diffusivity measurements.....	39
19. LFA diffusivity measurement and DSC specific heat measurement.....	40
20. Thermal conductivity calculated on the Laser Flash.....	41
21. Isotropic Half-Heusler	44
22. Anisotropic Bismuth Telluride.....	45
23. Cutting and rotating a texture dependent sample to prepare for a Laser Flash run	46
24. Sample put back together	47
25. Laser Flash comparison of the thermal conductivity of Bi_2Te_3 measured along different axis.....	48
26. Laser Flash and Low Temperature Thermal Conductivity comparison of the thermal conductivity of Bi_2Te_3 measured along the same axis	49
27. Netzsch Pegasus 404C® DSC	53
28. Specific Heat comparison of heating rates.....	56
29. PPMS and DSC specific heat comparison	57
30. Melting of Gold.....	59
31. Low Temperature and High Temperature Thermal Conductivity comparison.....	63

CHAPTER ONE INTRODUCTION

With looming thoughts about Earth's depleting energy, scientists have come together to investigate new ways of recycling and converting energy. One avenue to address our energy problem is thermoelectrics. Thermoelectrics have the ability to convert a temperature gradient to power, which is useful in automobiles, and deep space probes. In contrast, thermoelectrics also converts power to a temperature gradient, which is a promising replacement for the noisy, moving parts of a refrigerator. There are three main phenomena that contribute to the promise of thermoelectrics. These phenomena are centered around the Peltier and Seebeck effects.

The Peltier effect transfers an input voltage into a temperature gradient across two dissimilar materials (figure 1a). The Peltier coefficient is represented by Π , where

$$\Pi = \frac{Q'}{I}. \quad (1)$$

In equation 1, Q' is the heating or cooling rate and I is the electrical current. This effect is useful in many everyday objects such as the refrigerator. A refrigerator that runs on thermoelectrics will be more reliable and quieter due to the absence of moving parts. A current will be passed through the thermoelectric materials and one material will be cooled while the other side will be heated. This process is already being used in many automobiles. With a flip of a switch a seat can be cooled in the summer and warmed in the winter due to the advances of thermoelectrics

The Seebeck effect is the transfer of a temperature gradient to power as seen in figure 1b. It can be visualized by connecting two materials. The end of one material is

heated while the other material is cooled. This temperature difference creates a heat flow across the two samples due to the effect of excited electrons moving from the heated material to the cooled material. The heat flow leads to a potential difference, which is related to the temperature difference through the intrinsic Seebeck coefficient or thermopower (2).

$$\alpha = -\frac{\Delta V}{\Delta T} \quad (2)$$

Where α is the Seebeck coefficient of the sample, ΔV is the change in potential over the samples, and ΔT is the temperature difference. The change in potential is proportional to the change in voltage over the samples, which is measured in the low temperature resistivity and thermopower system, R&S, in the following way. The Seebeck coefficient or thermopower can be either positive or negative depending on the dominant charge carrier of the sample. The sample's thermopower is negative if electrons are the dominant carrier while the sample's thermopower is positive if holes are the dominant carrier. A sample with a negative Seebeck coefficient is deemed an n-type sample. Similarly a sample with a positive Seebeck coefficient is deemed a p-type sample. The Seebeck effect has great promise in conserving work and energy. For example in a Radioisotope Generator (RTG) the decay of certain isotopes creates a constant temperature difference of about 33K. Through the application of thermoelectric materials this temperature difference is converted into an electrical voltage, which is used to power the exploration probe. This is a major advancement in astronomy due to the fact that before the development of RTGs astronomers could not fuel a satellite to probe the solar system much past our neighboring planets.

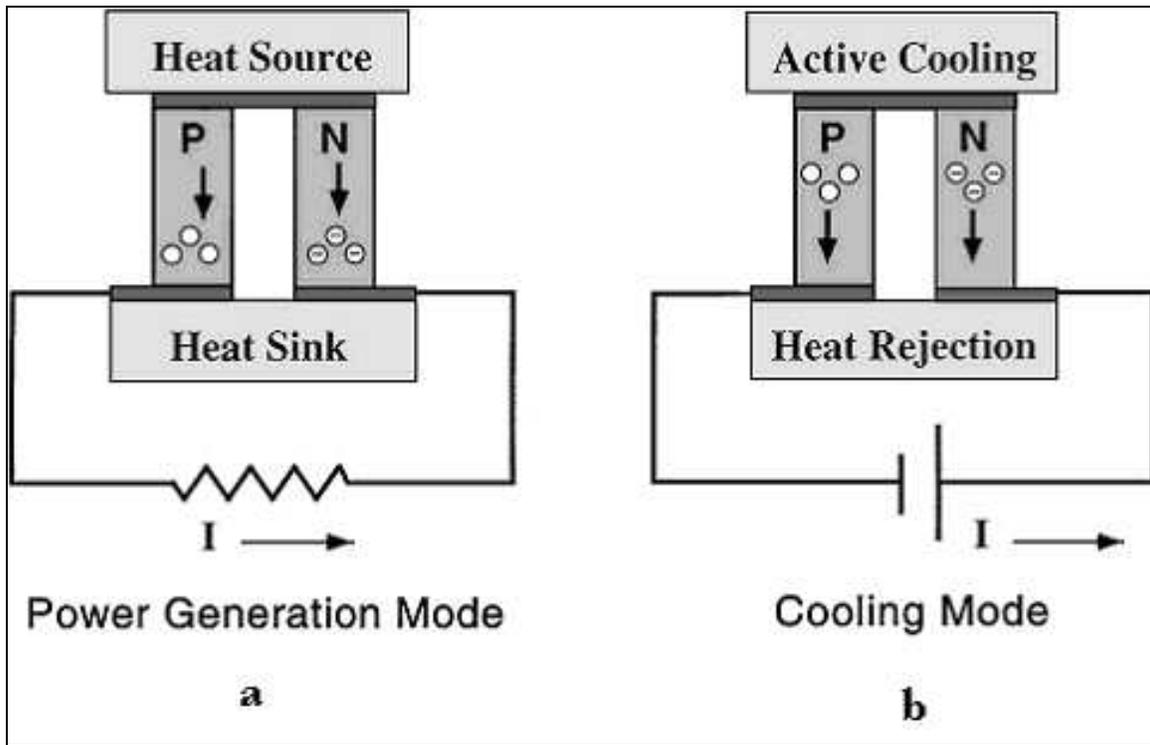


Figure 1. Thermoelectric Modules. (a) Seebeck Effect (b) Peltier Effect ¹

A material's potential for thermoelectrics is judged by the value of its figure of merit. The higher the figure of merit is for a sample the better the sample is at converting a temperature gradient to power and power to a temperature gradient. This value is dimensionless and based on different intrinsic parameters of a material.

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T \quad (3)$$

where ZT is the figure of merit, α is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. To optimize the ZT one attempts to increase the power factor (4) while decreasing the thermal conductivity.

$$PowerFactor = \alpha^2 \sigma \quad (4)$$

This is challenging due to the fact that the electrical conductivity is directly related to the thermal conductivity (5) through the Wiedemann-Franz Relationship, and as one variable increases or decreases the same thing happens to the other. However the thermal conductivity comprises of the lattice and electrical thermal conductivity as seen in equation 6.

$$\kappa_E = L_O T \sigma \quad (5)$$

$$\kappa = \kappa_E + \kappa_L \quad (6)$$

Where κ_E is the electrical thermal conductivity, L_O is the Lorentz number, and κ_L is the lattice thermal conductivity. By altering only the lattice contribution to the thermal conductivity the total thermal conductivity changes without affecting the electrical conductivity. As an example skutterudites allow for the insertion of rattlers, which alter the phonon movement within the sample and effectively decrease the lattice contribution to the thermal conductivity.

Each material has its own optimum temperature. For example Bismuth Telluride has a ZT around 1 at 400K, while Silicon Germanium has a ZT around 1 at 1200K (figure 2). As a result each material is tested for thermal conductivity, thermopower, and resistivity at different temperatures. To compensate for this large temperature range the Complex and Advanced Materials Laboratory (CAML) at Clemson University has a series of measurement systems that measure the properties of a material with different techniques at different temperatures. The thermal conductivity is measured by the Low Temperature Thermal Conductivity system, the PPMS Thermal Transport Option (TTO), and the Laser Flash, which measures at temperatures between 15 and 300K, 1.9 and 300K, and 300 and 1370K respectively. Similar temperature ranges are measured on different Resistivity and Thermopower systems in the lab.

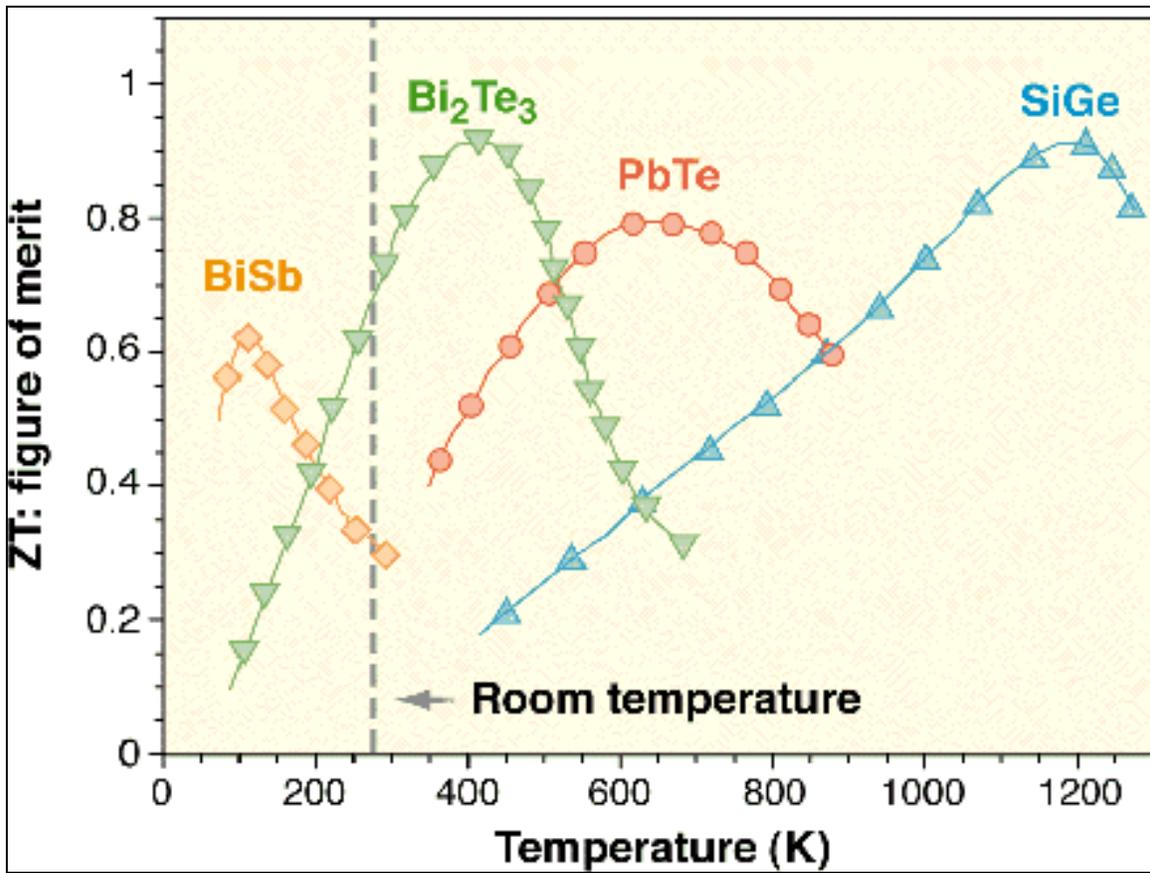


Figure 2. State of the Art Thermoelectric Materials ²

In summary a good thermoelectric material has a high figure of merit. It is important to optimize the power factor and thermal conductivity properties of the sample by doping the material, inserting rattlers, or engineering other effects. Many different elements will alter the structure of the sample and consequently increase or decrease the ZT. In this thesis the main focus is on various thermal conductivity measurements. There are three main methods that the Complex Advanced Materials Lab of Clemson University uses to measure a material's thermal conductivity. These techniques are (1) a customized steady state, low temperature thermal conductivity system, (2) a thermal transport option (TTO) on the Physical Properties Measurement System (PPMS), and (3) the high temperature LFA 457 MicroFlash (Laser Flash). Each system comes with its own set of advantages and disadvantages to measuring the thermal conductivity of certain samples but each is used to check the results against each other, which makes the lab's published data both accurate and reliable.

CHAPTER TWO LOW TEMPERATURE THERMAL CONDUCTIVITY

Experimental Procedure

Background

The low temperature thermal conductivity system is a customized system that runs up to two samples at a time. The system inputs power into the sample via a 120 Ω strain gauge (resistive heater) and graphs power vs. ΔT as shown in figure 3. The slope of this graph is the thermal conductance, an intrinsic property of the sample, due to the following equation.

$$P=K*\Delta T \tag{7}$$

By combining the thermal conductance with the dimensions of the sample, the thermal conductivity is calculated according to equation 8.

$$K=\kappa(A/L) \tag{8}$$

κ is the thermal conductivity, A is the cross sectional area of the sample, and L is the distance between the differential thermocouple that is thermally connected to the sample.

Most of the error in the low temperature thermal conductivity measurements is due to the uncertainty in the dimensional measurements; however, between 1 and 5% of the 10 to 15% uncertainty is due to the uncertainty in heat loss through the many components of the system. In order to keep this error as low as possible, concern is placed on the ability to reduce conduction and radiation in the system. By placing three radiation shields coated in gold around the sample puck radiation loss is kept to a minimum. Another way to reduce radiation is by considering the size of the sample. A long, thin sample has a high surface to

area ratio, which allows for more radiation loss. As a result samples are recommended to be as short and fat as possible. The data shows a basic trend of radiation loss at high temperatures. As the sample reaches temperatures close to 200K a significant amount of radiation is lost in some materials. This is easily corrected and is addressed in later sections of this paper.

Conduction is also addressed in the low temperature thermal conductivity system. First the type and size of the wires used on the sample is taken into account. By using 1mil thermocouples made of Constantan Chromega to measure the thermocouple voltage and phosphor bronze to measure the power input, both materials with low thermal conductivity, the power inputted into the sample is forced to flow through the sample and towards the heat sink.

Convection, the loss of heat through the system, is controlled through the use of a high vacuum pump. The system measures thermal conductivity in a pressure around 10^{-6} and 10^{-5} Torr.

Although there are many possibilities for uncertainty through radiation, conduction, and convection the methods previously described allow an estimate of less than 2% uncertainty.

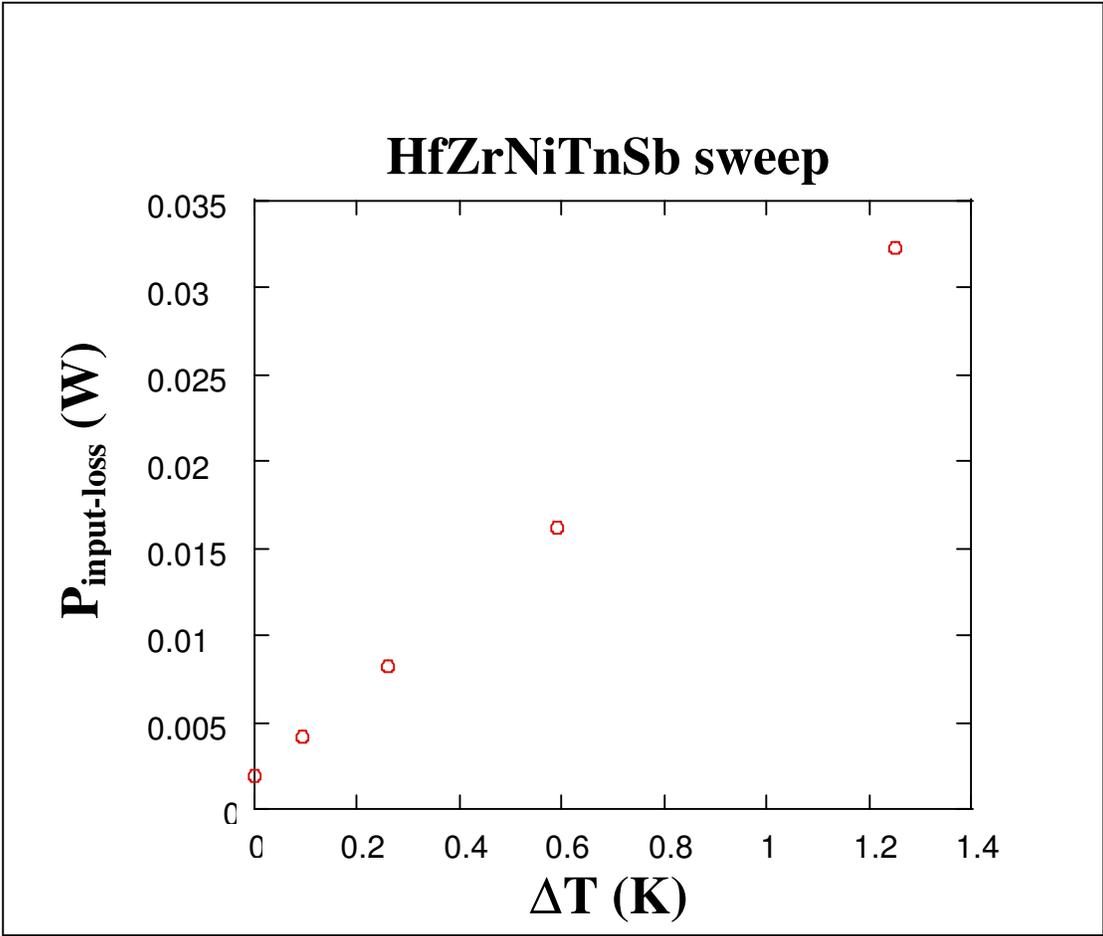


Figure 3. Power vs. Delta T Sweep

Experimental Apparatus

The low temperature thermal conductivity system consists of a custom made cryo-cooler head. This head houses the sample mount and is connected to an ultra high vacuum pump, a cryocooler, and lakeshore control system, power supplies, and meters that control the current and temperature of the system (Figure4). These devices are then connected to a computer that runs Lab View, an automated interface that allows the user to control the system and take and analyze data (5).

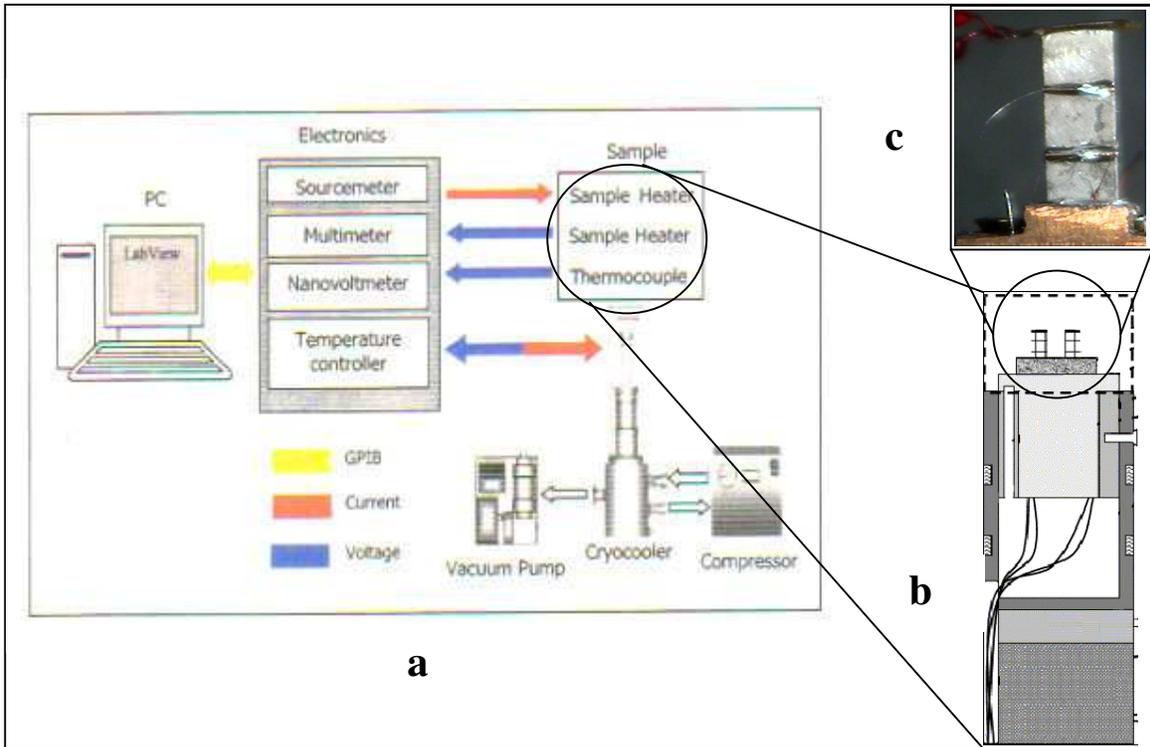


Figure 4. Thermal Conductivity System (a) Diagram of TC system³ (b) Cryocooler head⁴ (c) Mounted 2x2x8mm³ sample

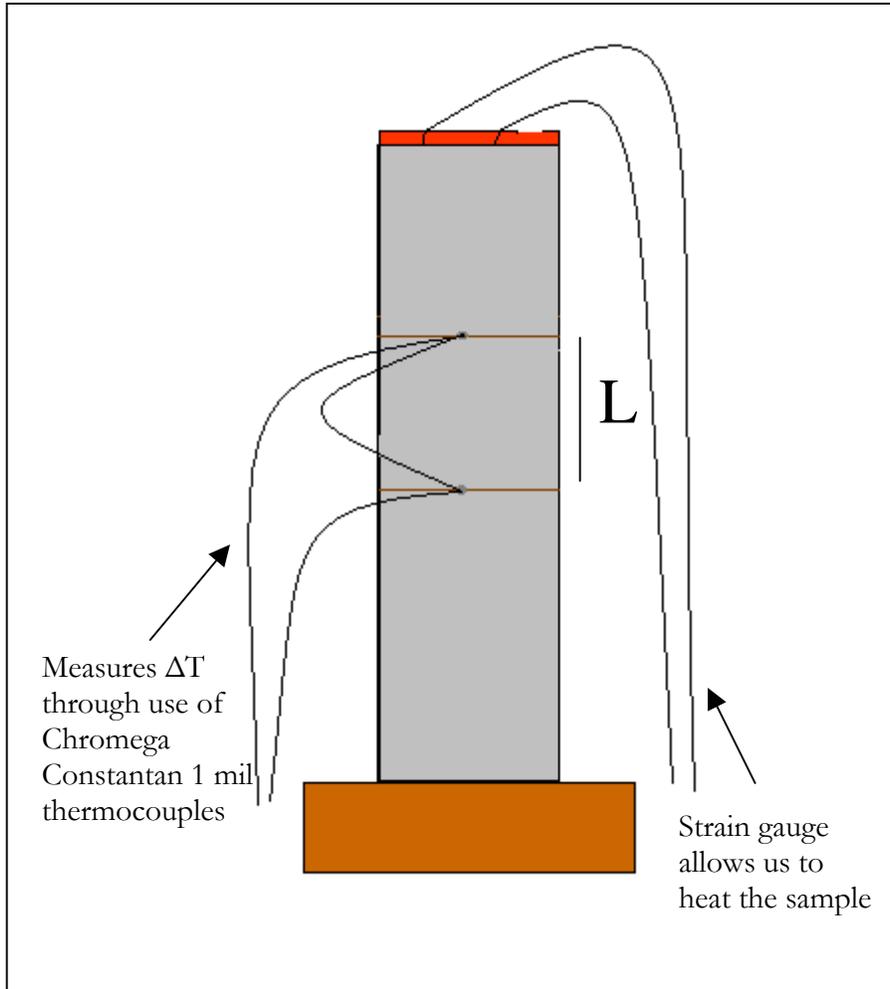


Figure 5. Sample mounted with thermocouple and heater wires attached.

Sample Mounting

Two 2mmx2mmx8mm, optimized for both the thermal conductivity and resistivity systems, samples are mounted to a standard thermal conductivity puck as seen in figure 5. This puck is a standard Quantum Design AC Transport puck with minimal adjustments. A copper plate also known as the heat sink is epoxied to the center of the puck using Stycast epoxy, which allows for thermal contact but minimizes electrical contact. Onto this copper plate two smaller copper blocks are screwed in, each to hold a sample, which allows maximum contact and easy removal.

Each block has a depression the same width and thickness as the sample and 1.25mm deep. This depression allows the end of the sample to be surrounded by copper and solder, allowing for maximum heat flow down the sample and into the heat sink. High temperature Lead Tin, PbSn, solder holds the sample as vertical as possible while sunk into the depression.

As figure 6 shows, the sample is fitted with two insulated #38 copper wires. These wires are epoxied using Stycast Epoxy to the sample about the sample's thickness away from each other but centered on the sample. The copper wires are epoxied as close to parallel to each other and as perpendicular to the sample as possible. By placing the wires such allows the temperature reading to be consistent across the width of the sample. Copper wire is used in order to read a uniform temperature across the sample. The exposed part of the copper wire is scraped and a junction of a Constantan Chromega thermocouple is soldered to the copper wire using high temperature PbSn solder. Constantan Chromega thermocouples are used because they have a low thermal conductivity thus minimizing conduction. The ends of the thermocouple are soldered to the puck using the same solder.

The pins of the puck allow the system to measure the voltage across the thermocouple and through calibration files are able to determine the change in temperature across the sample.

On the top of the sample a 120 Ω strain gauge resistive heater is glued using 5 Minute Epoxy. The insulated wires extending from the heater are cut to size and scraped at the ends. A #42 Phosphor Bronze insulated wire is cut to size and its ends are also scraped. The PBz end is then soldered to the tip of the heater wire using PbSn solder. The solder is then coated in nail polish in order to reinsulate the ends. The opposite end of the PBz wire is soldered to the puck in order to connect to complete the circuit. This process is repeated for the other heater wire.

If the sample is a porous sample that the solder will not adhere to further preparation is required. A sample such as Bismuth Telluride, Bi_2Te_3 , whose unit cells are spaced so that the sample is porous, cannot be in direct contact with solder. The solder tends to diffuse into the sample and create a false thermal conductivity reading. To avoid this contamination, the sample must first be nickel plated, which is done with a 6-8V power source and a taper-tipped Nickel plating pen. The nickel is then scraped off the sample where it is not needed in order to prevent an alternate heat flow. The Nickel plating creates a diffusion barrier, allowing the solder to remain on the surface of the sample and not affect the thermal conductivity reading. Once Nickel plated, the sample is ready to begin the process of mounting, described in the previous paragraphs. Nickel plating is also often used with high oxidation samples. Because PbSn solder does not stick to the oxidized layer, the layer is first removed and the sample is immediately plated. This prevents further oxidation while creating a more adhesive sample surface.



Figure 6. Low Temperature Thermal Conductivity Mount⁴

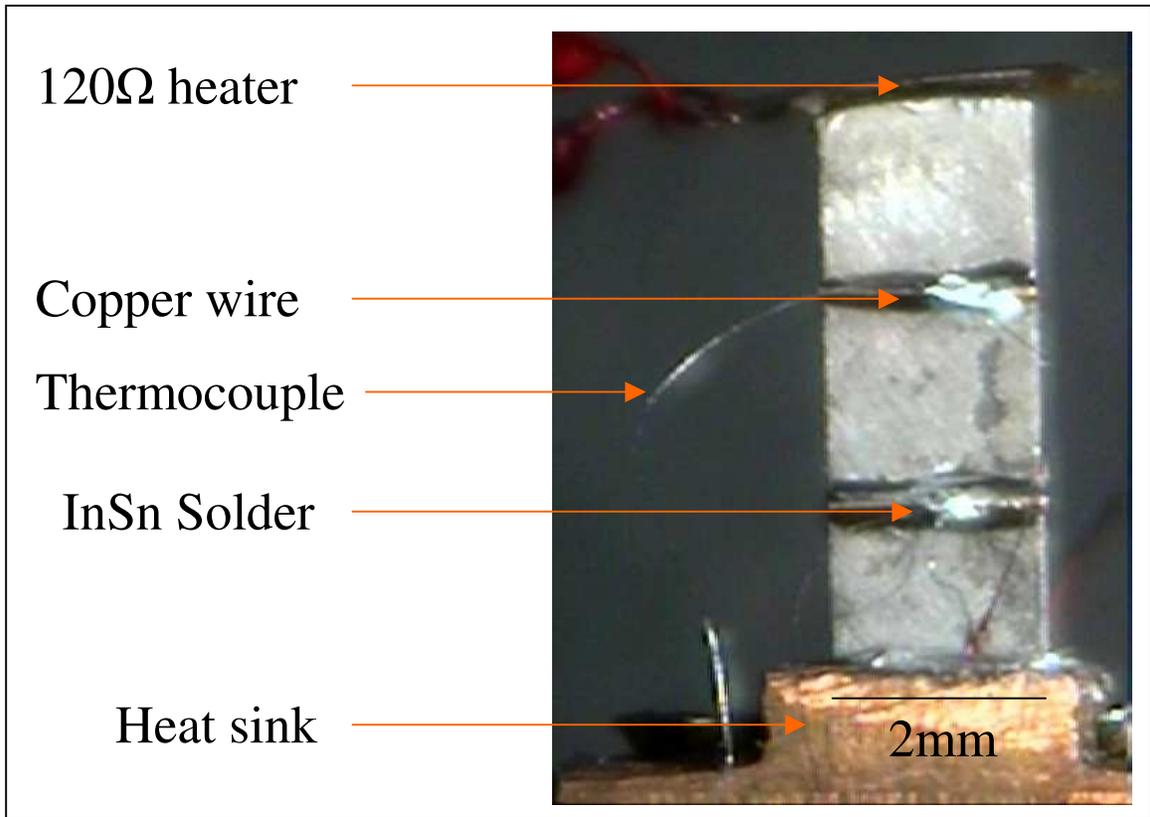


Figure 7. Sample Mounted for Low Temperature Thermal Conductivity Runs

Experimental Results

As sample measurements are taken there are a few things that need to be considered. Because most thermoelectric research is interested in decreasing the lattice thermal conductivity it is often necessary to split the thermal conductivity data into its electrical and lattice components. To do this, the resistivity of the sample is found on another set of systems, customized low temperature R&S. The resistivity data (figure 8) is indirectly proportional to the electrical conductivity.

$$\sigma = \frac{1}{\rho} \quad (9)$$

Where σ is the electrical conductivity and ρ is the resistivity. Once the electrical conductivity is calculated it is graphed with respect to temperature. The graph is smooth fit on Kaleidagraph (figure 9). This smooth fitting allows the temperature points graphed on the low temperature thermal conductivity system to be present on the σ vs. T graph. This is necessary because the R&S system typically takes 800 points over the same temperature range as the thermal conductivity system, which typically takes between 30 and 60 points depending on the settings. Once the curve is smooth fit these 30 to 60 points are established and used to find the electrical thermal conductivity. According to the Wiedemann-Franz Relationship the electrical thermal conductivity is equal to the Lorentz number, approximately $2.3 \times 10^{-8} \text{ W}\Omega/\text{K}^2$, times the electrical conductivity times the temperature.

$$\kappa_e = L_o \sigma T \quad (10)$$

After calculating the electrical component of the thermal conductivity the lattice contribution is calculated. Because the low temperature thermal conductivity system measures the total thermal conductivity, which is the electrical and lattice components

$$\kappa = \kappa_e + \kappa_L \quad (11)$$

the lattice component can be found with the following equation.

$$\kappa_L = \kappa - \kappa_e \quad (12)$$

The comparison of the three graphs can be seen in figure 10.

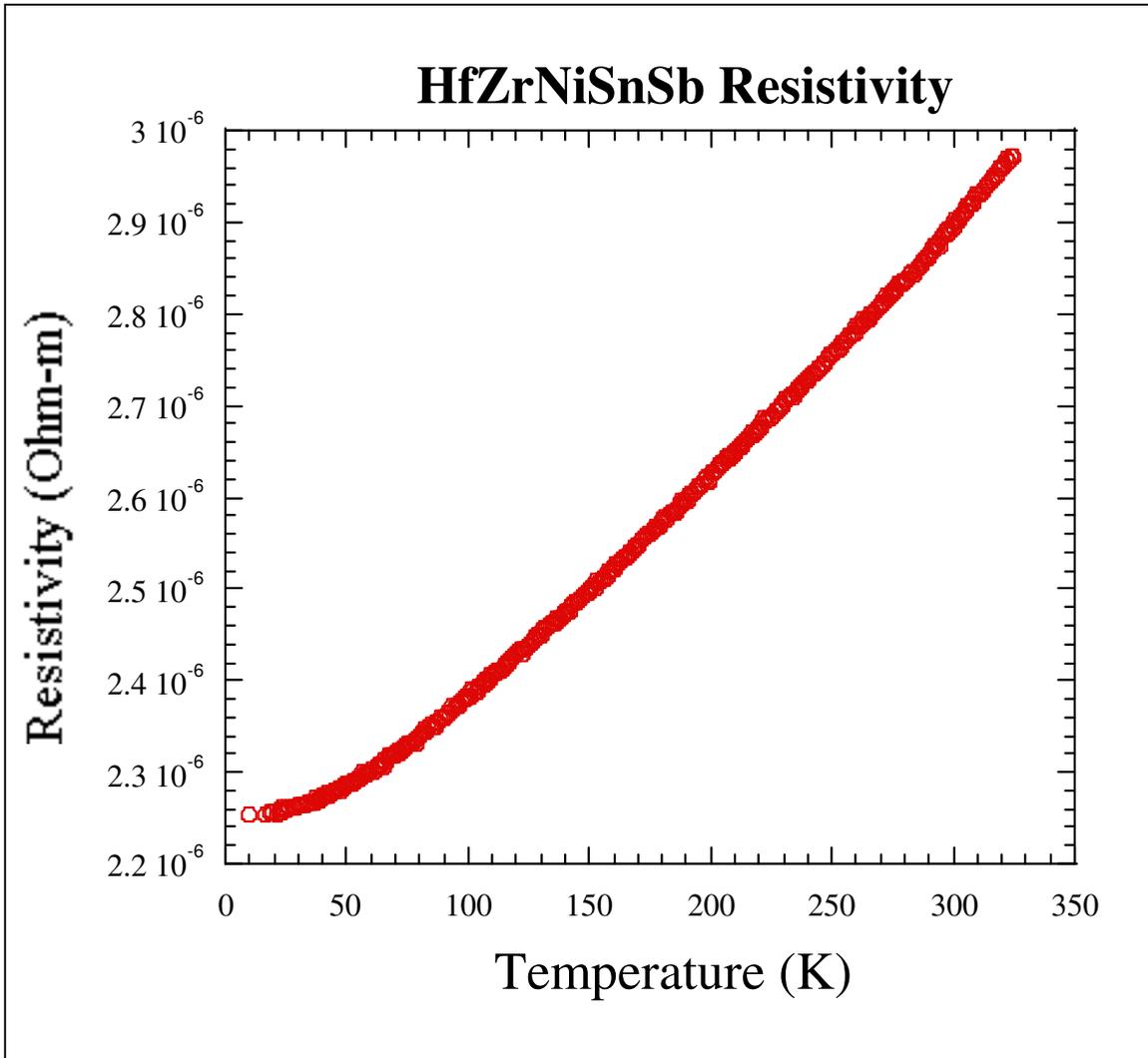


Figure 8. Resistivity vs. Temperature of HfZrNiSnSb

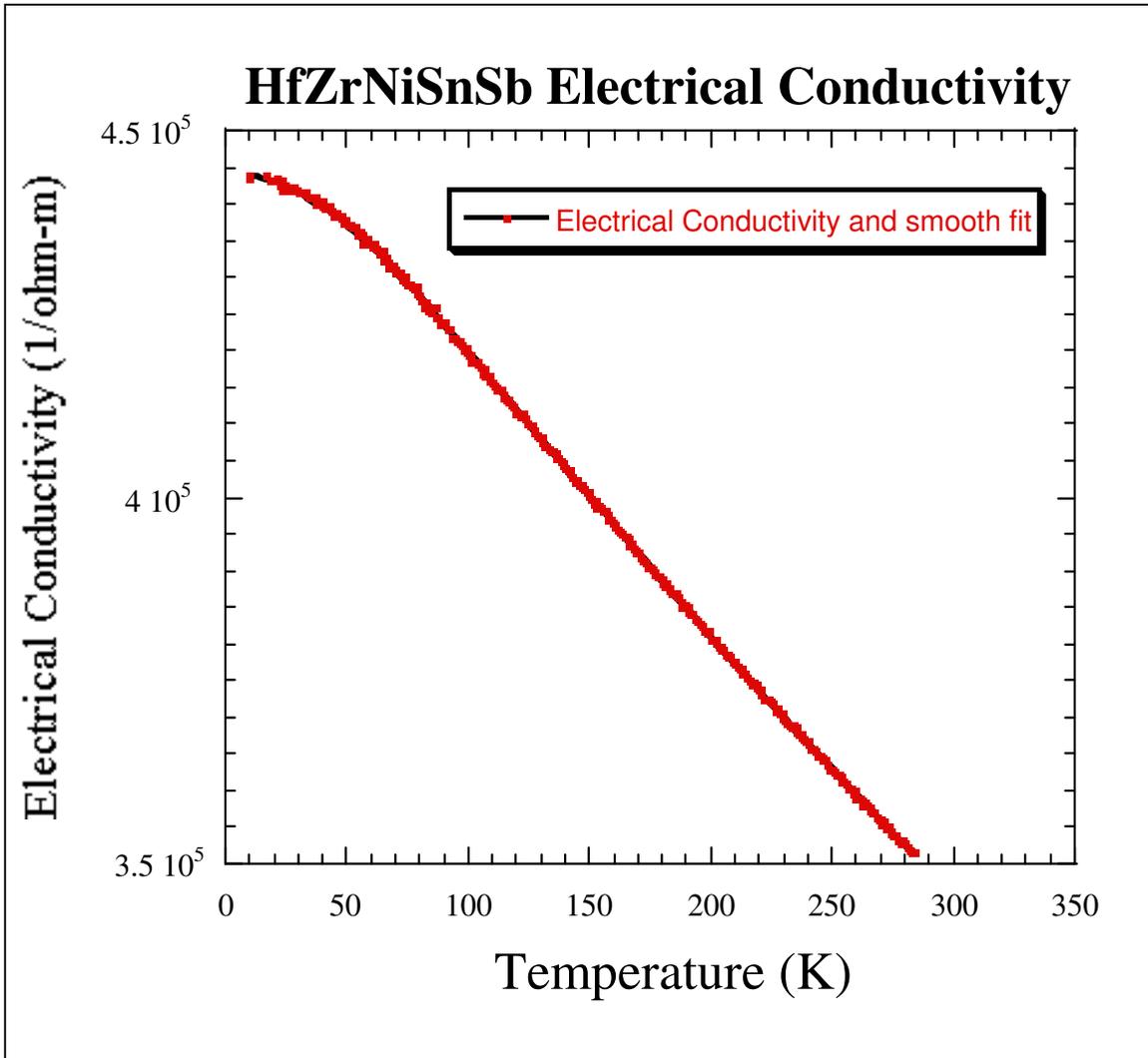


Figure 9. Smooth fit Electrical Conductivity vs. Temperature of HfZrNiSnSb

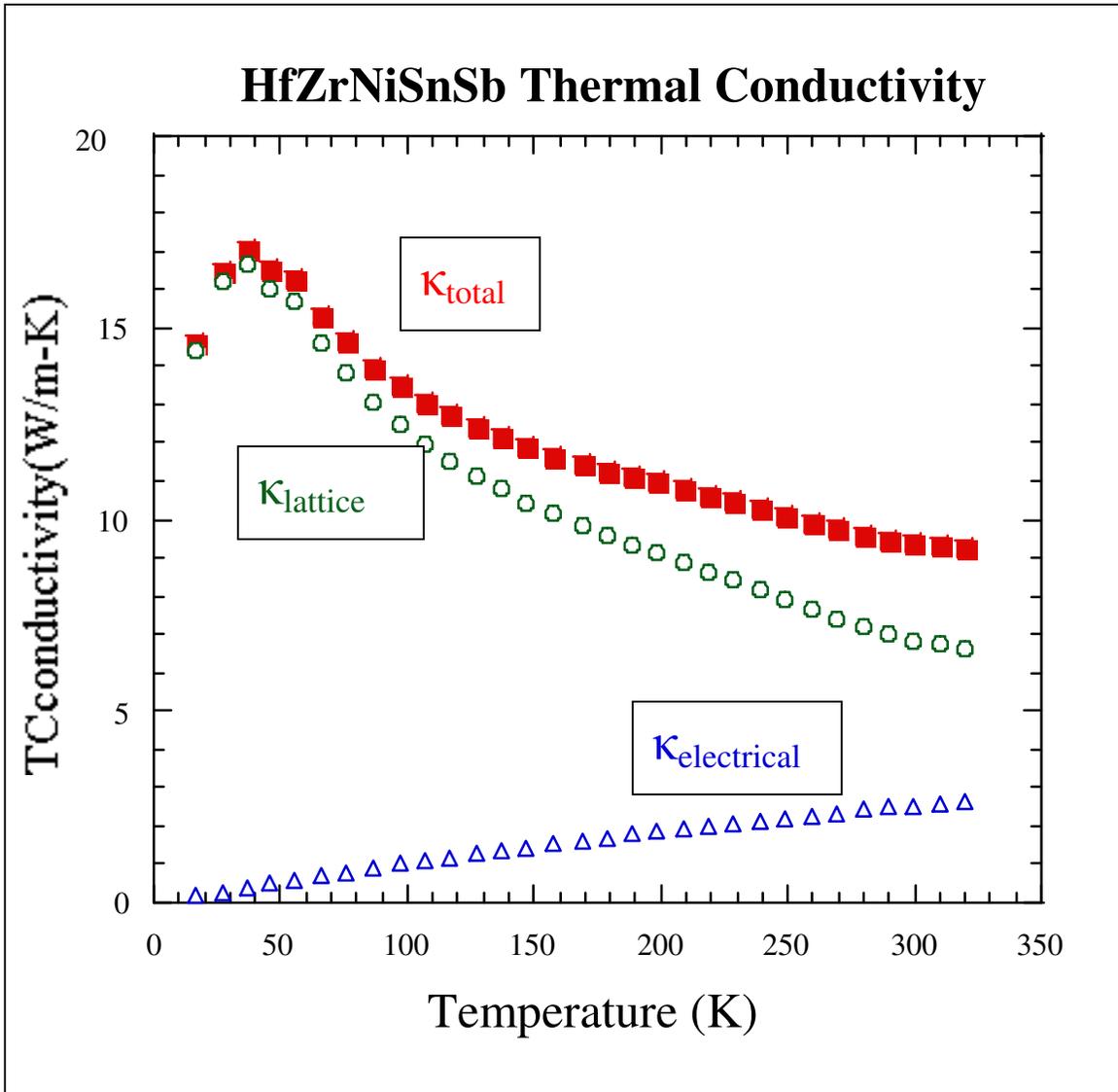


Figure 10. Comparison of total, electrical, and lattice thermal conductivities in HfZrNiSnSb

By comparing the resulting graph, lattice thermal conductivity vs. temperature, theories are made about the lattice effect of certain dopings or substitutions within the sample. For example, in Half-Heusler materials, substituting Hafnium for Zirconium reduces the lattice thermal conductivity, which in effect should increase the ZT of the material as long as the electrical conductivity remains constant (figure 11). The substitution of Hafnium, a heavier element than Zirconium, causes the atoms of the material to be dissimilar in mass. Now as the phonons pass through the sample they are scattered by the heavier atoms, causing the lattice thermal conductivity to decrease.

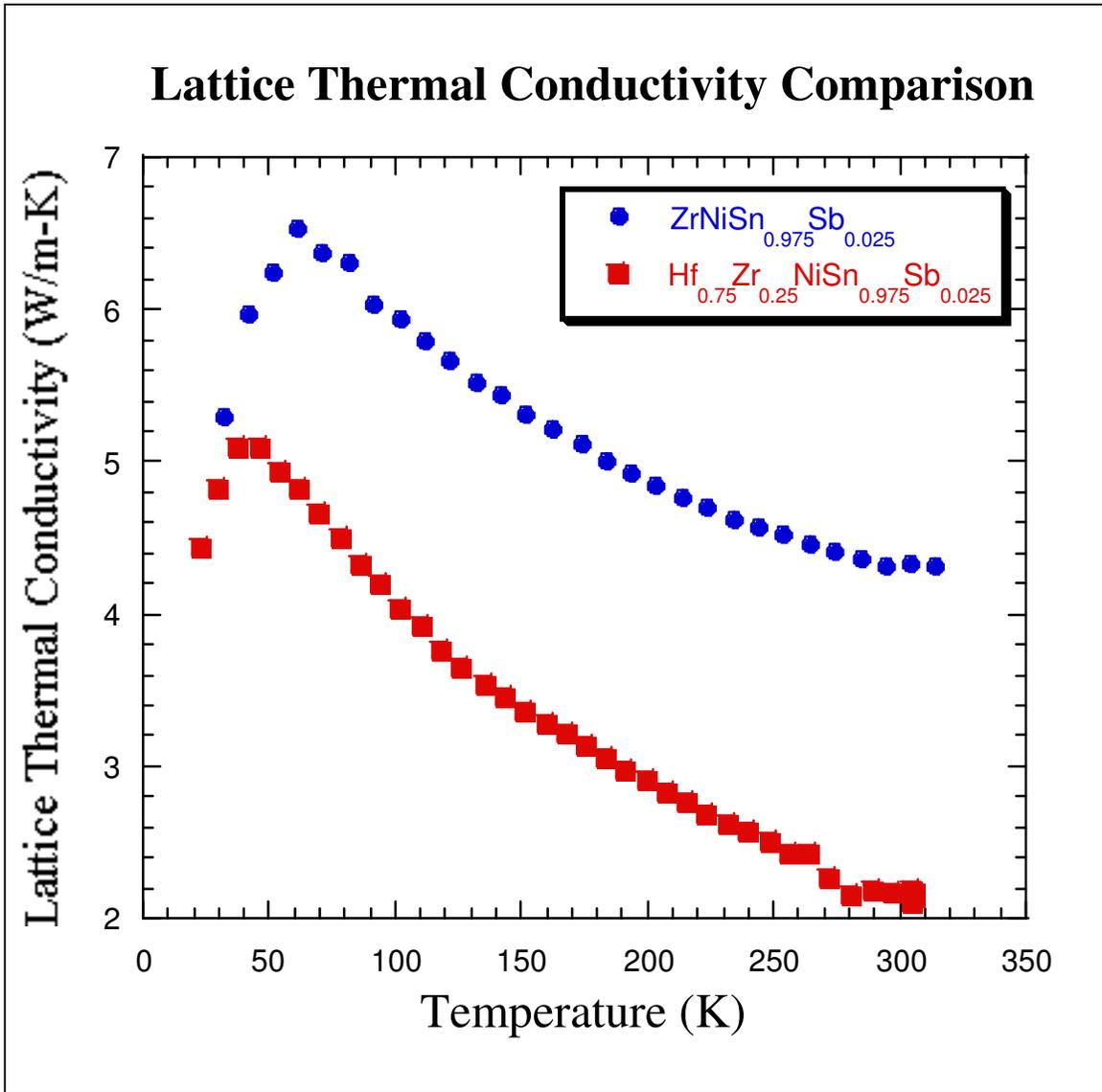


Figure 11. Lattice thermal conductivity comparison between $\text{ZrNiSn}_{0.975}\text{Sb}_{0.025}$ and $\text{Hf}_{0.75}\text{Zr}_{0.25}\text{NiSn}_{0.975}\text{Sb}_{0.025}$

Another matter that must be considered is the presence of a radiation tail at high temperature in low thermal conductivity materials. This tail normally begins around 200K depending on the sample size and can be spotted by its upward trend. Radiation loss is proportional to T^3 and is represented by the following equation.

$$P_{RAD} = A\gamma^2 \epsilon(T^4 - T_s^4) \quad (13)$$

Where P_{RAD} is the power radiated from the sample, A is the cross sectional area, γ is the Stephen-Boltzmann constant ($5.7 \times 10^{-8} \text{ W/m}^2\text{K}^4$), ϵ is the emissivity, T is the temperature of the sample, and T_s is the temperature of the system. Knowing that

$$T_s = T + \Delta T \quad (14)$$

a Taylor expansion of

$$\begin{aligned} T_s^4 &= (T + \Delta T)^4 \\ &= T^4 + 4T^3\Delta T \end{aligned} \quad (15)$$

gives

$$P_{RAD} = A\sigma^2 \epsilon(4T^3\Delta T) \quad (16)$$

A radiation correction can be seen in figure 12.

Because radiation goes as temperature cubed the change in lattice thermal conductivity versus the temperature cubed should produce a linear graph (Figure 13). Up to higher temperatures the graph is fairly linear. However, at temperature close to room temperature and above the linearity changes. This is due to the fact that Bismuth Telluride is bipolar at high temperatures, meaning that there is a contribution by both the holes and electrons in the sample.

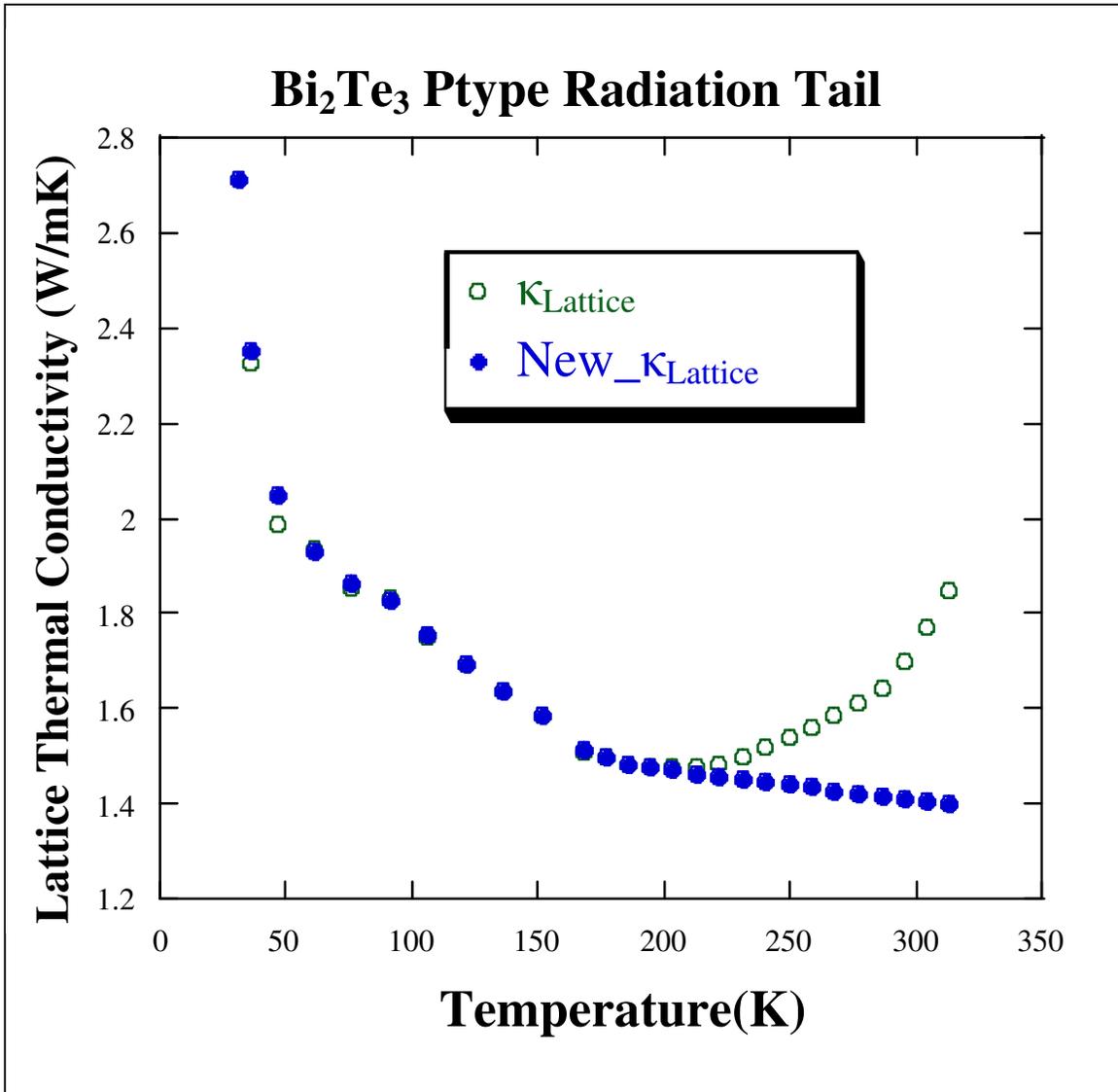


Figure 12. Radiation tail present in Bi₂Te₃

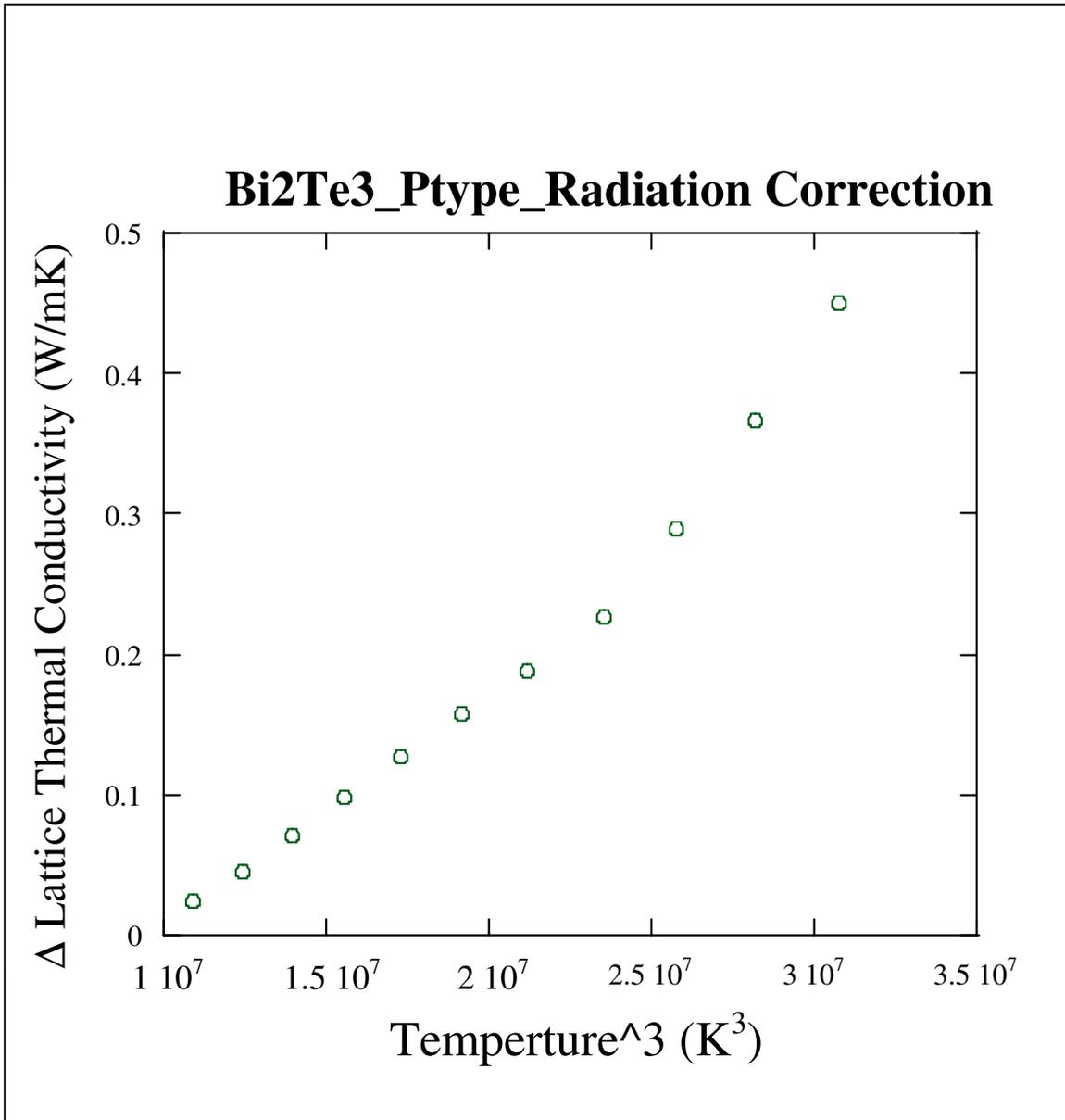


Figure 13. Linearity of the change in lattice thermal conductivity vs. temperature³

CHAPTER THREE LASER FLASH AND DIFFERENTIAL SCANNING CALORIMETER

Laser Flash

Experimental Procedure

Background

Netzsch designed the LFA 457 MicroFlash® to be the leader in modern laser flash technology. This apparatus allowed for thermal diffusivity measurements up to a higher temperature regime than the other systems. The LFA 457 is capable of measuring the thermal diffusivity of a sample from 300 K to 1370 K. As the name suggests, the Laser Flash flashes a laser into a sample and measures the rate the heat emits from the sample. Using this data and the half-time equation, mentioned later, the thermal diffusivity of a sample is found. Using equation 17 the thermal conductivity is calculated.

$$\kappa = D\rho C_p \tag{17}$$

where κ is the total thermal conductivity, D is the thermal diffusivity, ρ is the sample density, and C_p is the heat capacity.

Experimental Apparatus

As mentioned before, the Laser Flash measures thermal diffusivity by pulsing a laser beam into one side of a sample and measuring the rate of heat passing through the sample. This will be described in more detail later in this chapter. As seen in figure 14 the Laser Flash is comprised mainly of a laser, a furnace, and an IR detector, which are controlled by the data acquisition program known as LFA measurement. A sample coated in graphite is

placed in a sample puck, which fits into a sample carrier (Figure 15). This sample carrier can carry three smaller sized samples or one large sample. As the Laser Flash acquires data it is automated to rotate the sample carrier in order to measure three samples at once.

Once the samples are loaded into the system, the Laser Flash is vacuumed for three minutes and then purged, with Argon gas. This procedure is done twice. The second time the system is purged the valve on the system is open and the flow rate is reduced to 75mL/min. Argon continuously flows through the system during the run. Argon is used because it is an inert gas and will not react with any of the samples that run in the system.

As the system is vacuumed and purged the operator loads the Laser Flash program, which is located on a PC that is connected to the system, and enters the required data. This data is helpful in remembering important facts about the samples. Most importantly though, it is used to translate the heating rate, temperature points, and frequency of data points to the system as well as determine the thermal diffusivity and conductivity of the sample by the insertion of the thickness, specific heat, and density of the sample.

During a measurement the system increases in temperature and stabilizes within a set number of degrees from a fixed temperature. The laser then sends a flash of light that reflects off of a mirror and is sent into the sample, which is placed perpendicular to the flash. The radiation shields are present to prevent any radiation loss before the laser hits the sample. When the laser penetrates the sample its particles are excited causing a temperature rise at the other end of the sample. An infrared detector measures the temperature rise with respect to time and sends this information to the PC. The radiation that is emitted from the sample is then cooled by liquid nitrogen that is contained in the dewer. A curve that best fits a graph proportional to the change in temperature vs. time is graphed and its data is used to

find the thermal diffusivity of the sample (Figure 17). A series of best fit curves are available on the program but in the materials lab at Clemson University the types of samples measured are best fit by a curve called Cowan + pulse correction.

From the Cowan + pulse correction data, the half time is estimated and used in the following way (Figure 16). Because the temperature and detector data are proportional, the Laser Flash program calculates the maximum detector signal and cuts it in half. At this point on the graph there is a corresponding time. This time is called the half time. Using the half-time method (equation 18) the thermal diffusivity is calculated.

$$D = 0.1388 \frac{d^2}{t_{1/2}} \quad (18)$$

Where D is the thermal diffusivity, d is the sample's thickness, and $t_{1/2}$ is the half time. By measuring the density, ρ , and specific heat, C_p , of the sample the thermal conductivity, κ , is extrapolated using the following equation.

$$\kappa = DC_p \rho \quad (19)$$

The data from the Laser Flash will be discussed in a following section.

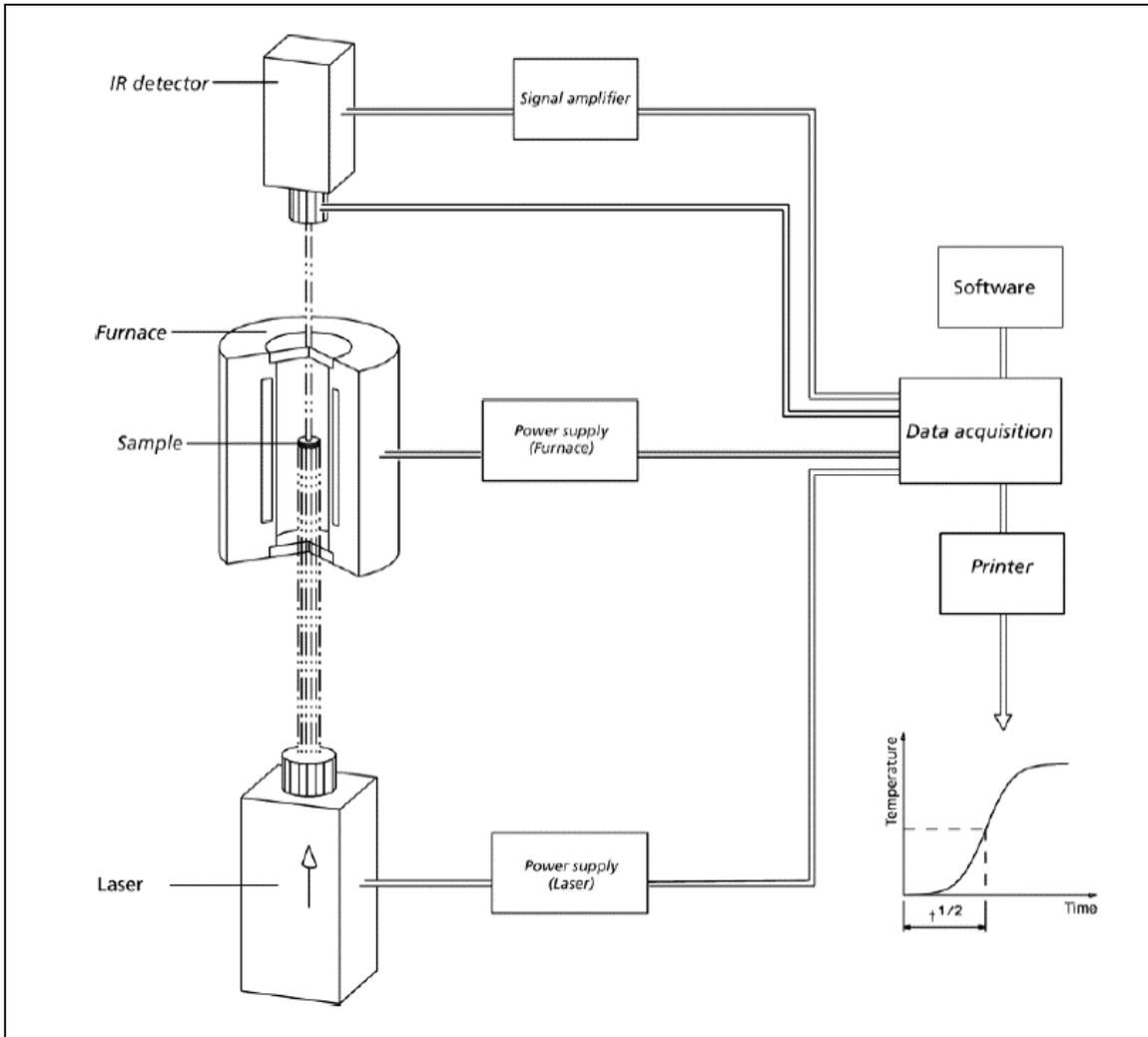


Figure 14. Laser Flash diagram⁵

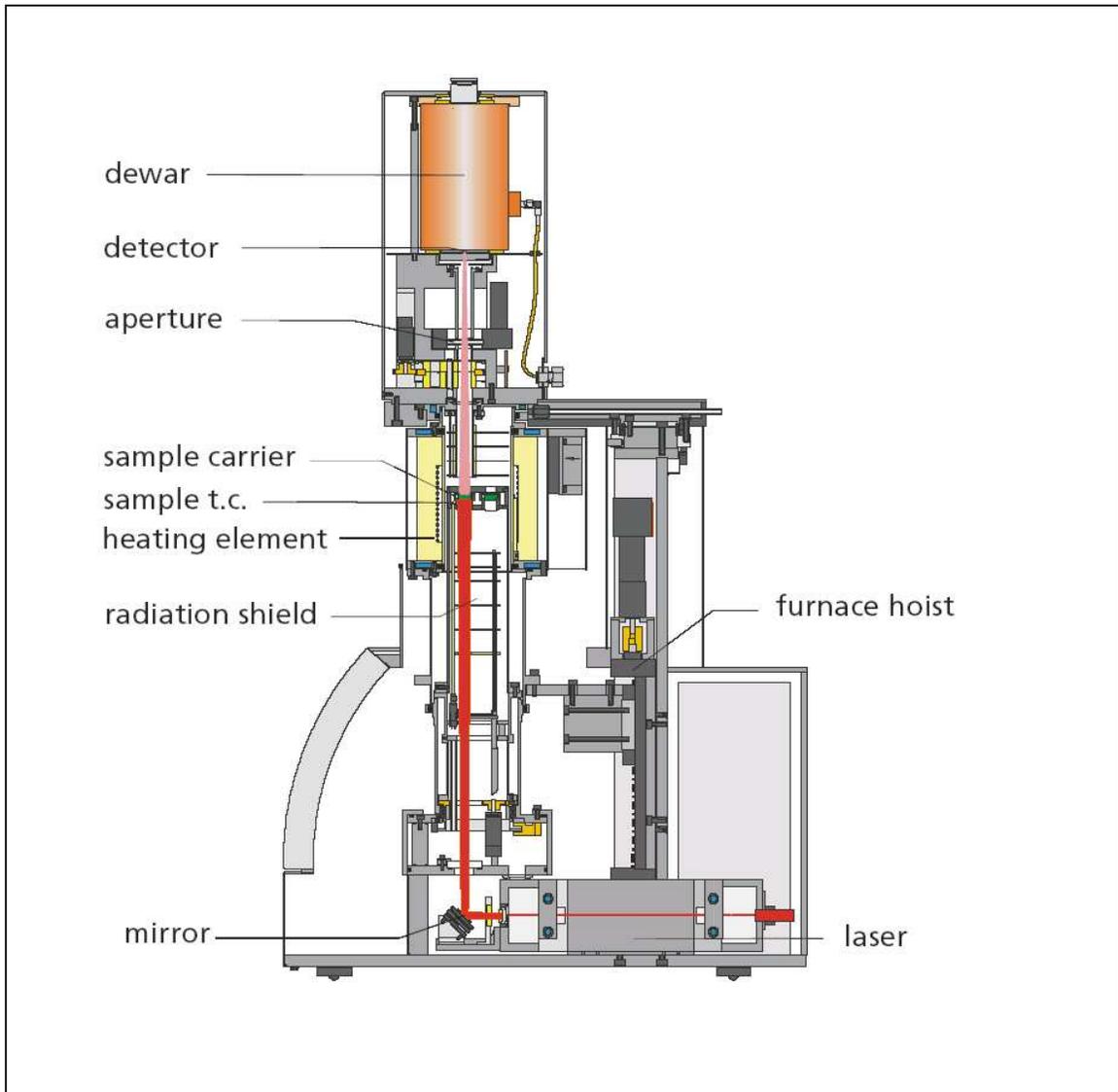


Figure 15. Netzsch LFA 457 MicroFlash ®⁵

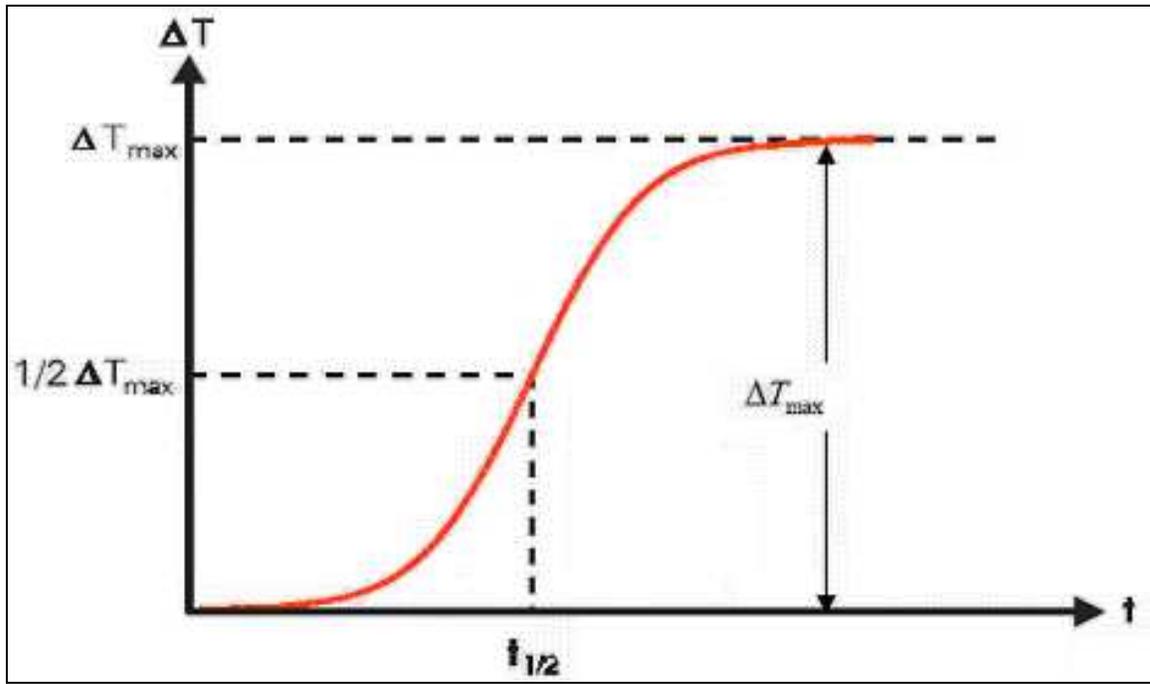


Figure 16. Half-time Method⁵

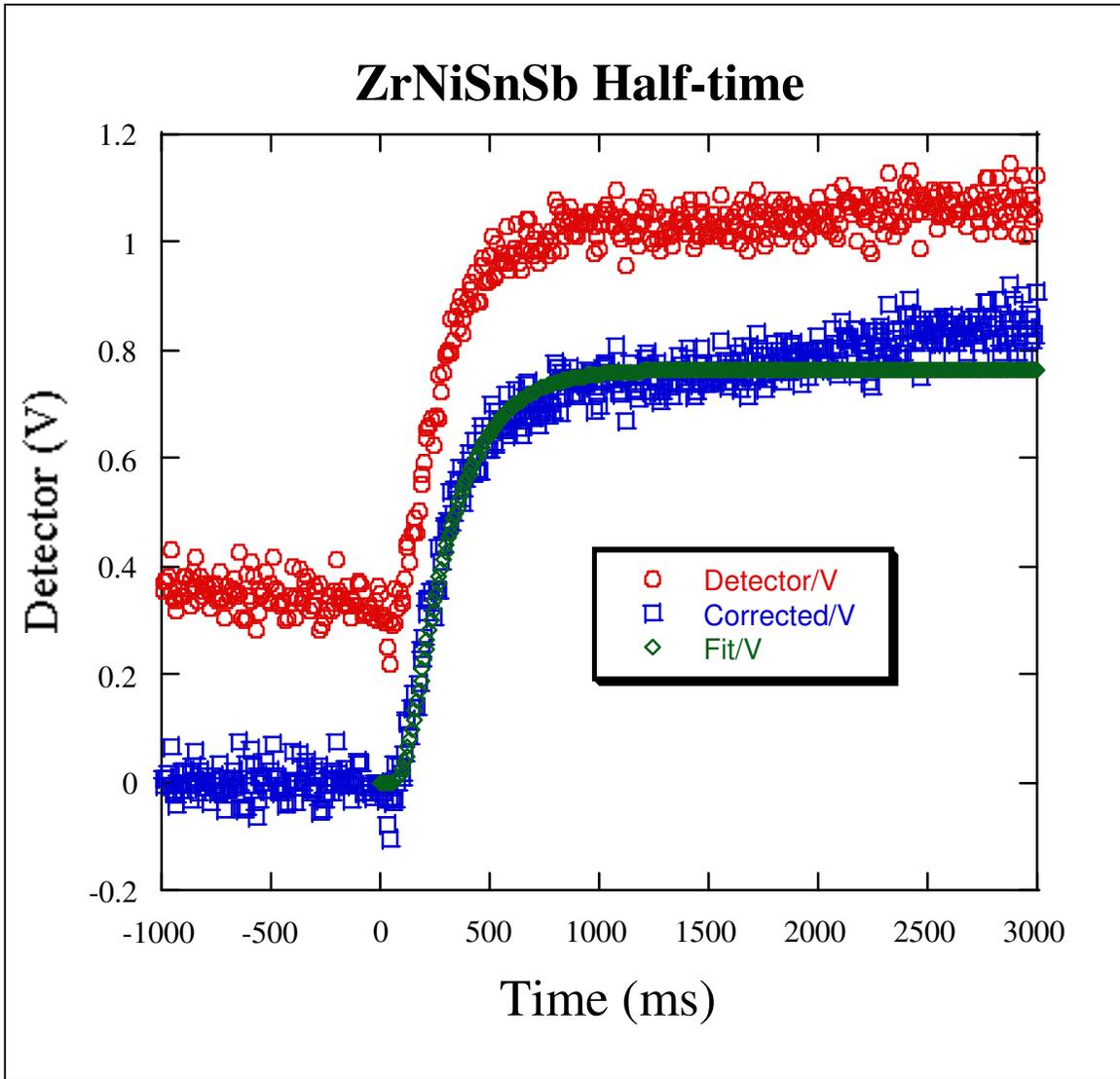


Figure 17. Half-time of ZrNiSnSb sample measurement

Sample Mounting

The Laser Flash can measure a range of sample sizes. These samples are then placed in their respective sample holders and placed into the sample tray, which houses three small samples or one large sample. This tray is automated to move each sample over the laser during the running. This allows the run to be quicker and more efficient.

The samples can be both square and circular, and should have a thickness around 2mm, although the system allows for a thickness ranging from 0.1mm to 6mm. This is advantageous due to the fact that outside systems require certain dimensions that the Laser Flash adheres to. If the sample is square it must be 8mm x 8mm or 10mm x 10mm. If the sample is round it can be 10mm, 12.7mm, or 25.4mm in diameter. The sample should be as flat as possible due to the fact that the laser flash should enter the sample at a 90 degree angle in order to assure a uniform heat flow through the sample.

If the sample is reflective in the slightest it is coated with a graphite spray. This is necessary so that the laser will not radiate off the sample's surface and all of the light will travel through the sample. The spray is applied until it is certain that no light will be reflected by the surface. The sample is then placed into its proper sample holder and the sample holder is fitted onto the sample tray, which is positioned in the system with the help of grooves located on a quartz shield that protects the series of radiation shields directly under the samples. Both holder and tray are made of Silicon Carbide and graphite, which are dull materials with little reflectivity. If the sample tray that holds three samples is not completely utilized, covers are placed over the openings preventing any light from filtering through.

Experimental Results

The results of the Laser Flash are both reliable and reproducible within 5% when measuring thermal diffusivity (Figure 18). However, because many dimensional and specific heat uncertainties are difficult to lower, the total thermal conductivity uncertainty of the Laser Flash is between 5 and 15%. This is comparable to the low temperature TC system and TTO option on the PPMS.

As previously mentioned the Laser Flash measures the change in temperature over time of the sample and consequently calculates the thermal diffusivity using the half-time equation. In figure 19 the thermal diffusivity is graphed vs. temperature. By combining the Differential Scanning Calorimeter's (DSC) specific heat and the density of the sample the thermal conductivity is found (Figure 20).

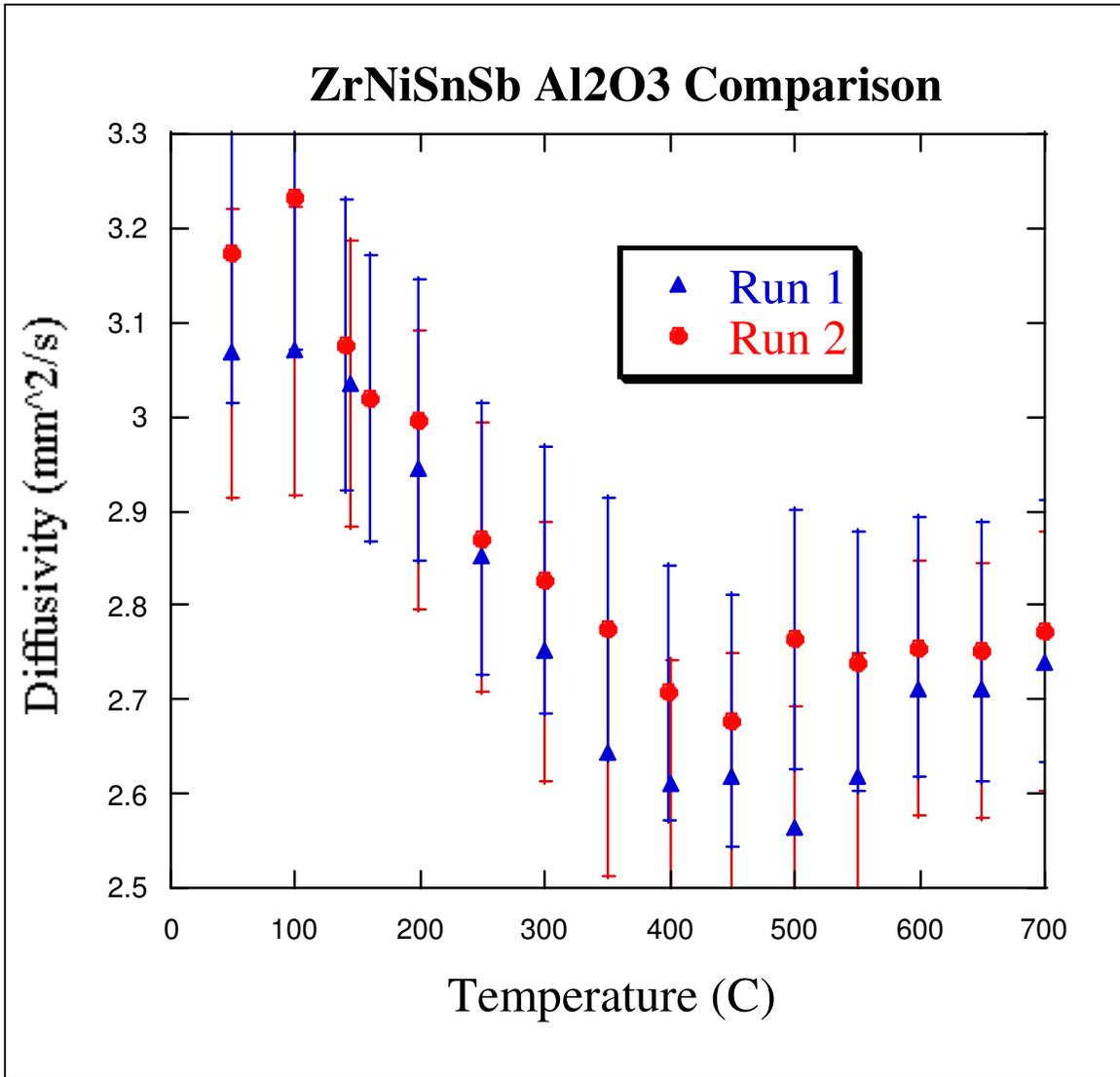


Figure 18. Reproducibility of thermal diffusivity measurements

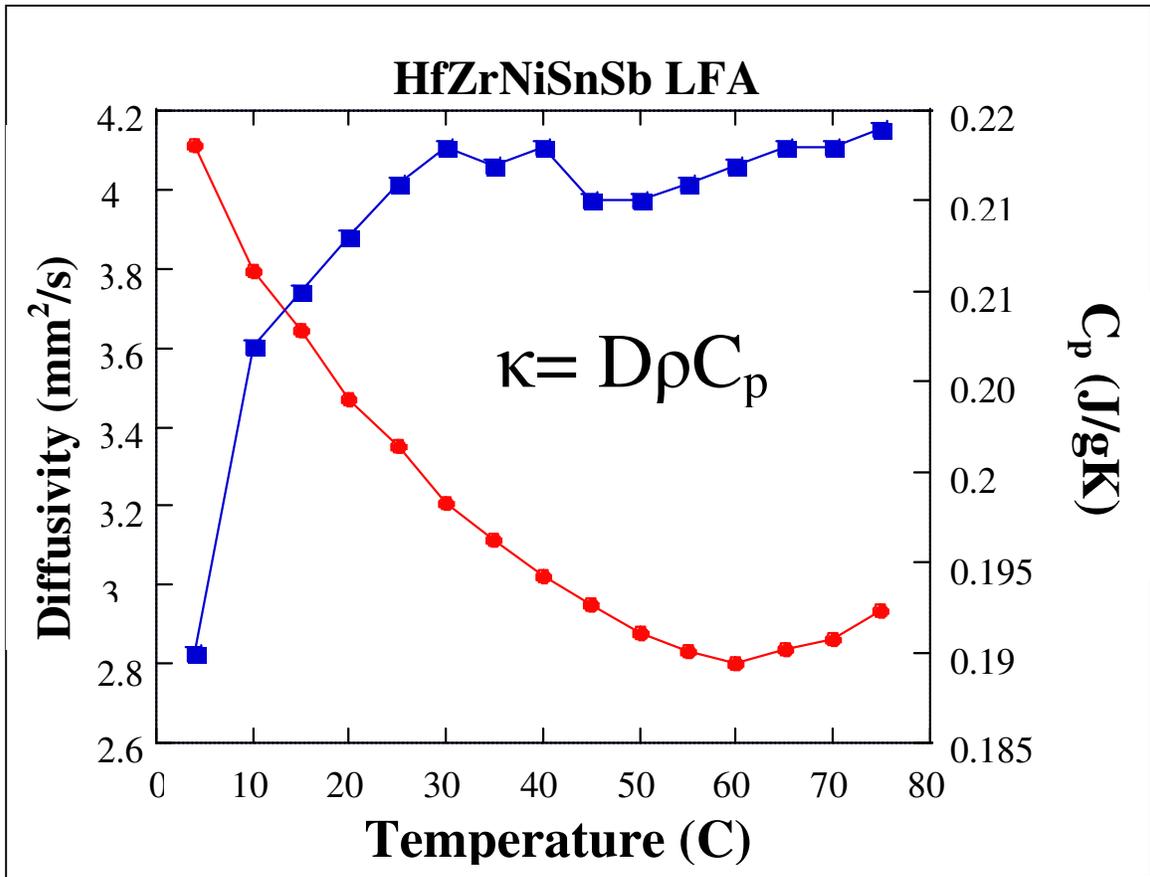


Figure 19. LFA diffusivity measurement and DSC specific heat measurement

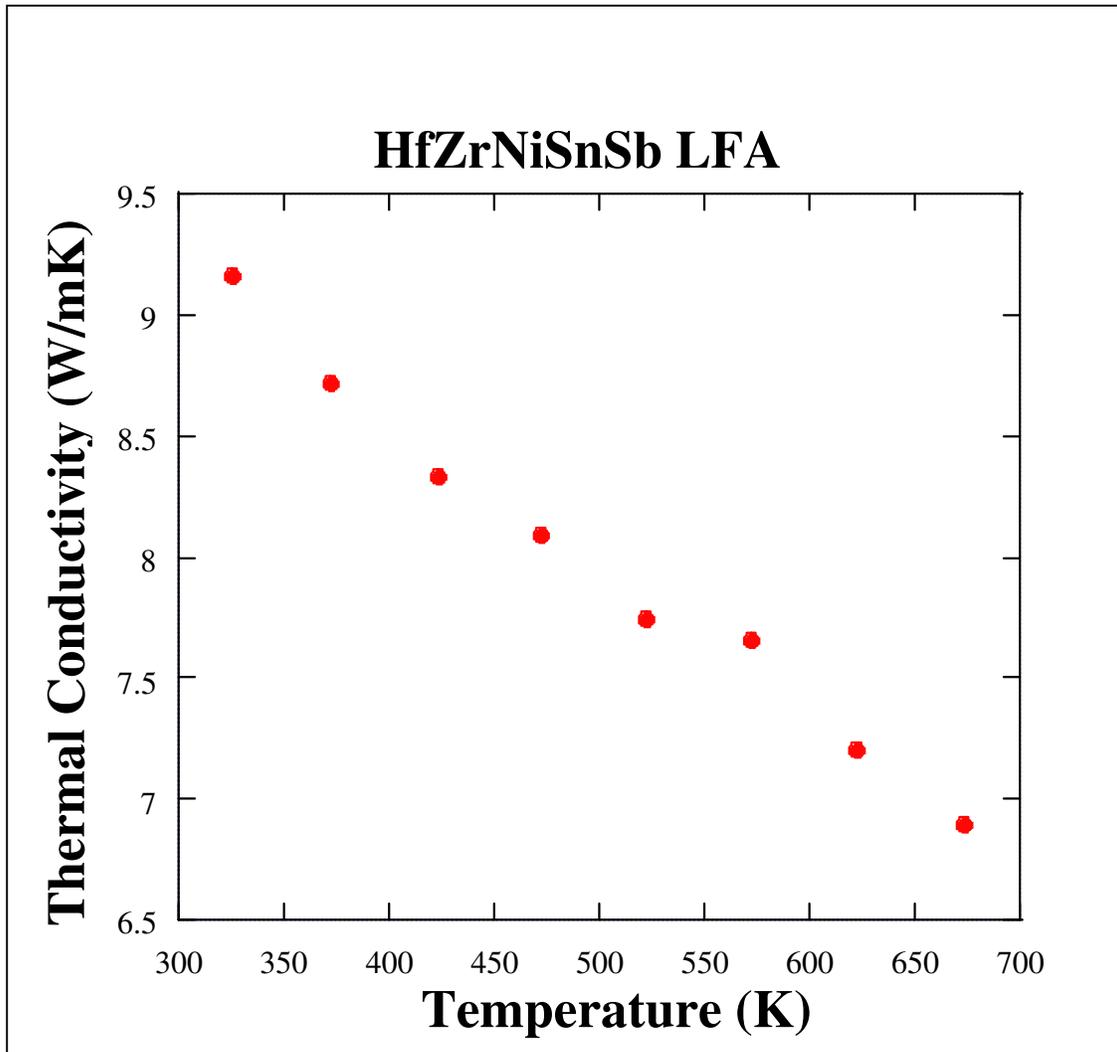


Figure 20. Thermal conductivity calculated on the Laser Flash

Due to the way the laser hits the sample it is necessary to be aware of the lattice parameters of the material. In figure 20 the sample measured is a Half Heusler, which is a cubic sample with a uniform a, b, and c axis length (Figure 21). As a result the axis the laser hits the sample at is ambiguous. However, in other materials such as Bismuth Telluride, because the laser hits the sample perpendicular to the sample it is important to determine the axis in which the thermal diffusivity should be measured. Because the Laser Flash and low temperature thermal conductivity systems are used to validate one another, the direction of measurement must be consistent. The low temperature thermal conductivity measures thermal conductivity along the 8mm length of the sample. The Laser Flash calculates the thermal conductivity across the thickness of the sample, which is usually around 2mm. As a result the two measurements are not measured across the same axis and in essence are not comparable for anisotropic samples.

To get around this obstacle the Bismuth Telluride sample was cut into four 2mm width samples. These samples were then rotated 90 degrees and glued back together using a minimal amount of epoxy as seen in figures 23 and 24. As a result the Laser Flash could calculate the thermal conductivity of the sample along the same axis as the low temperature thermal conductivity system could. The thermal diffusivity difference between the axis measurements was greater than 30% (Figure 25). After the realignment of the samples, however, the low temperature and high temperature thermal conductivity measurements matched within 2% uncertainty (Figure 26).

Analyzing the graph found in figure 26 implies that there are different contributions to the thermal conductivity data at different temperatures. As previously stated the thermal

conductivity is the addition of the electrical and lattice thermal conductivity. According to Wiedemann-Franz relation the electrical thermal conductivity has the following relationship.

$$\kappa_e = L_o \sigma T \quad (20)$$

The lattice thermal conductivity, however, is dependent upon the specific heat (C_p) and the phonon mean free path (l_p).

$$\kappa_l = \frac{1}{3} C_v v_s l_p \quad (21)$$

Below 50K the phonons are not making a significant contribution to the thermal conductivity due to the amount of energy available for the excitation of the phonons at this temperature. As a result the slope at this temperature is mainly due to the specific heat of the material. Between 50 and 300K the thermal conductivity is following the trend of the phonons. At these temperatures the specific heat begins to stabilize, allowing a minimum amount of contribution to the data. Above room temperature the bi-polar effect can be seen (Figure 26). As a result the thermal conductivity quickly rises with temperature, creating a faux radiation tail.

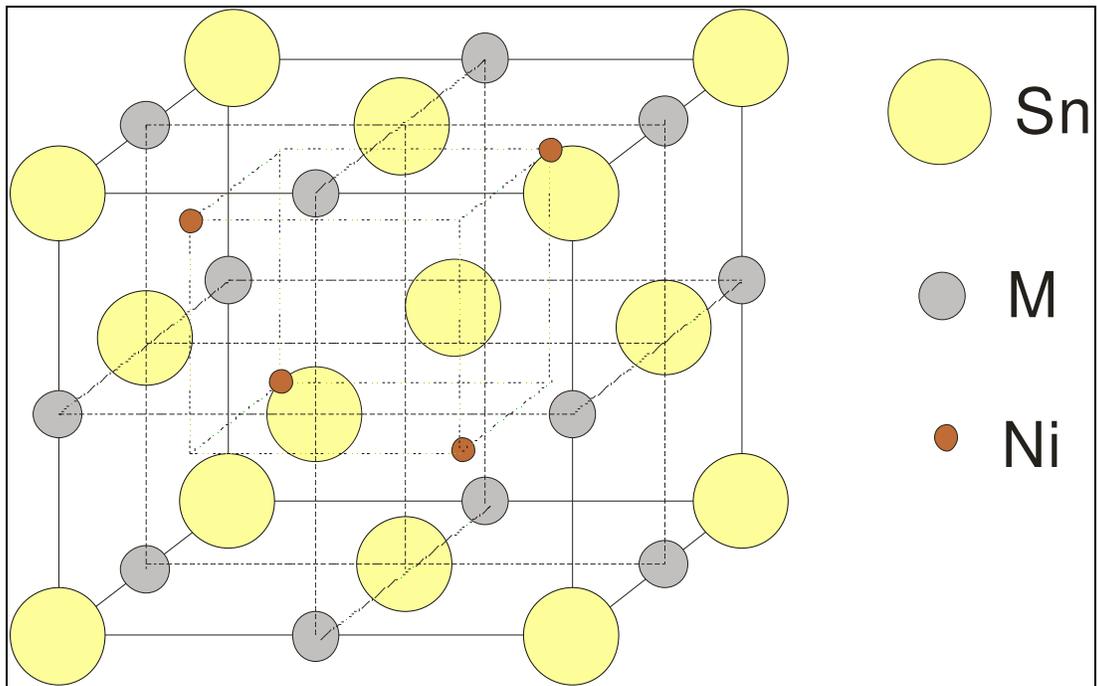


Figure 21. Isotropic Half-Heusler

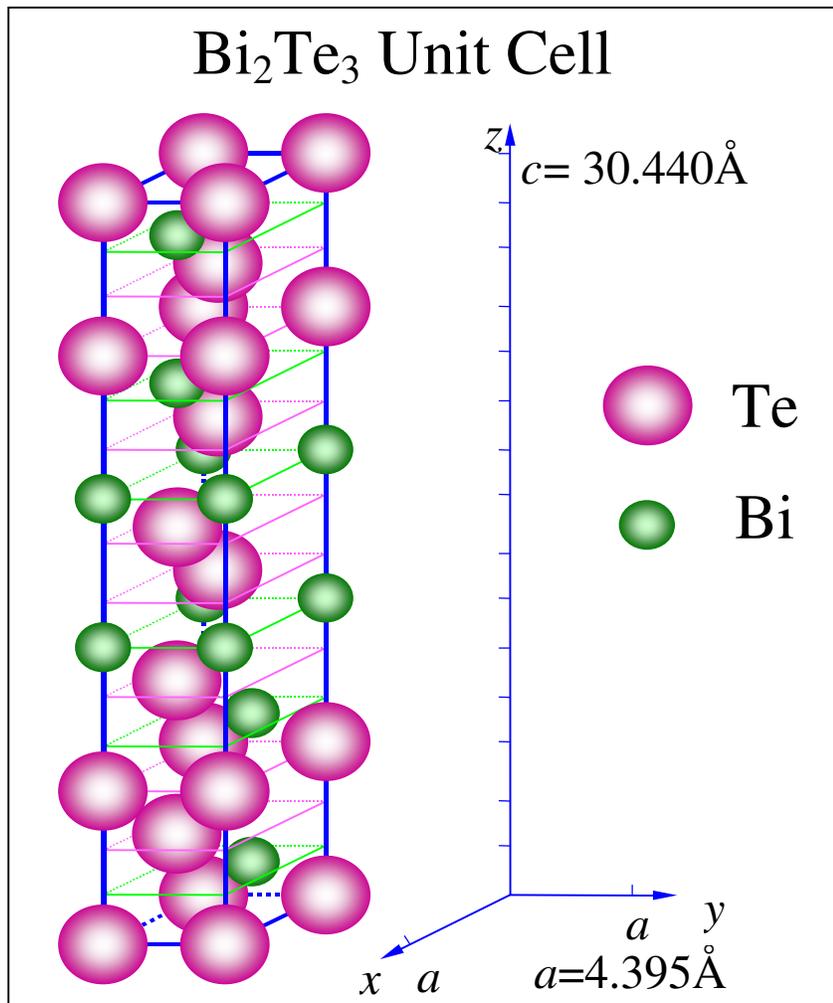


Figure 22. Anisotropic Bismuth Telluride⁶

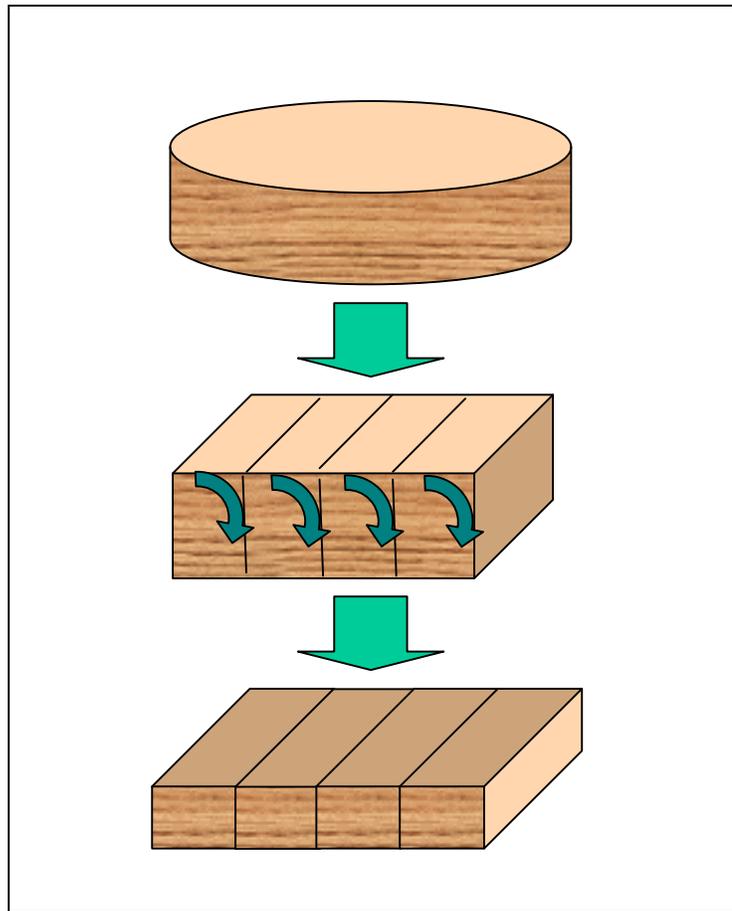


Figure 23. Cutting and rotating a texture dependent sample to prepare for a Laser Flash run⁶

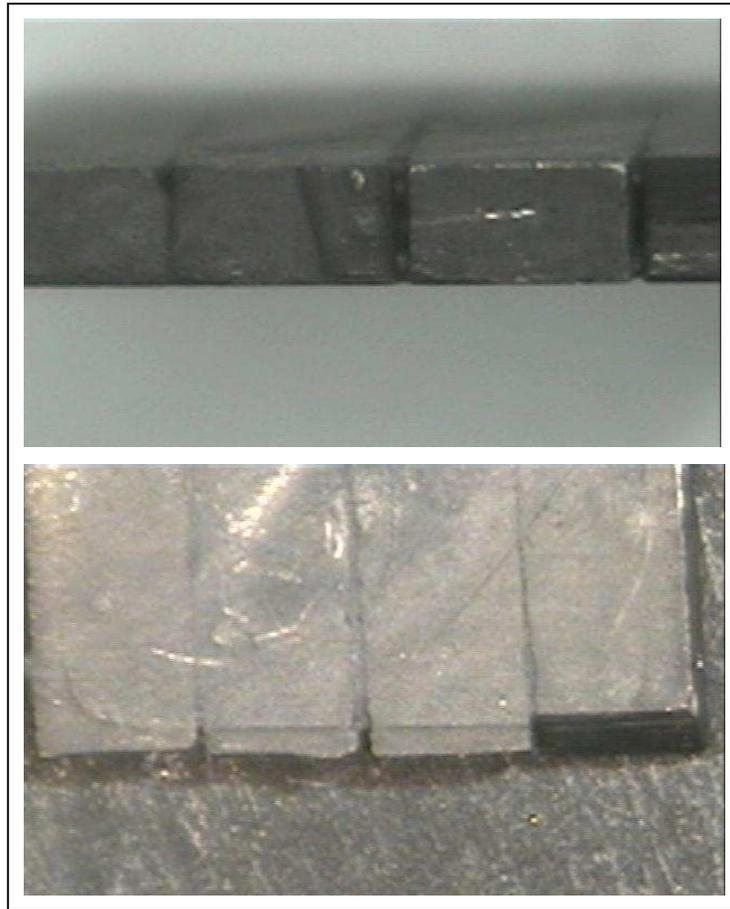


Figure 24. Bi_2Te_3 Sample put back together

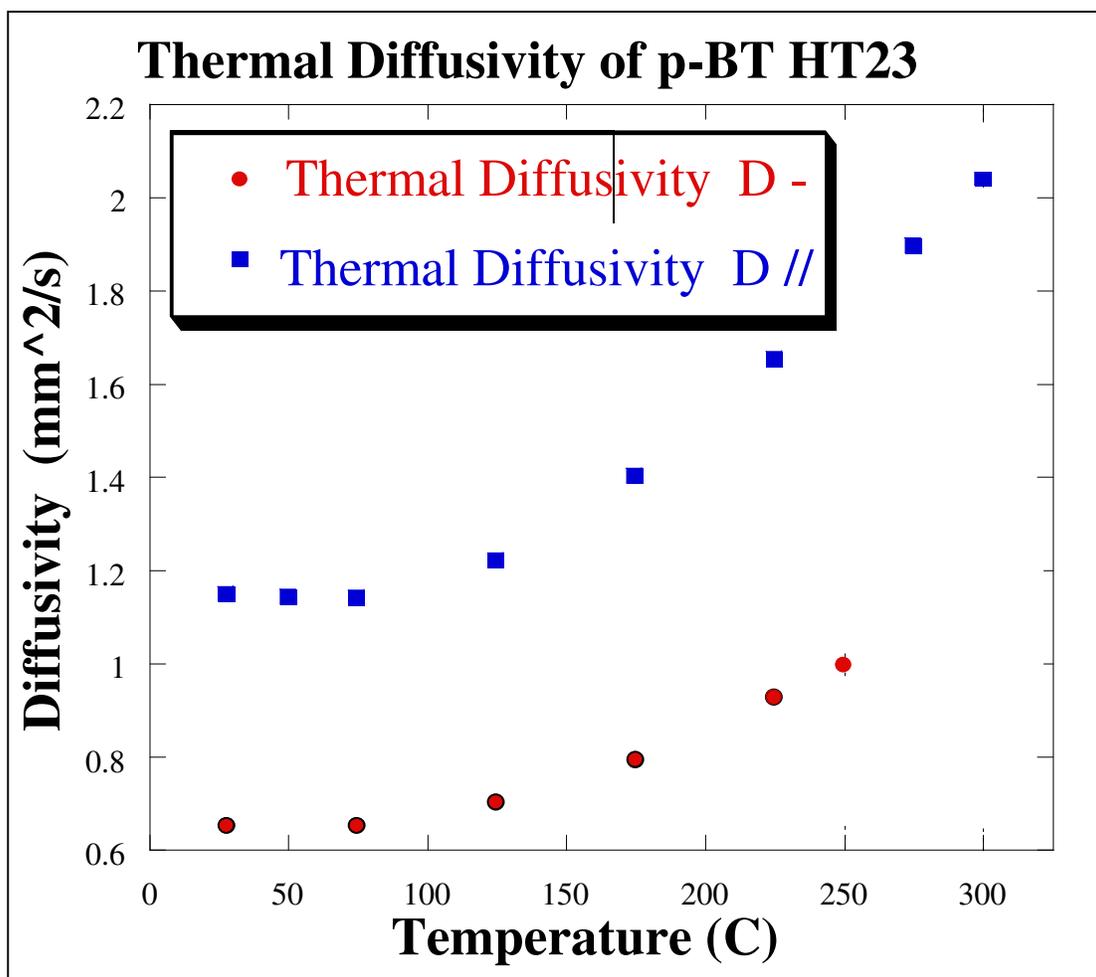


Figure 25. Laser Flash comparison of the thermal conductivity of Bi₂Te₃ measured along different axis

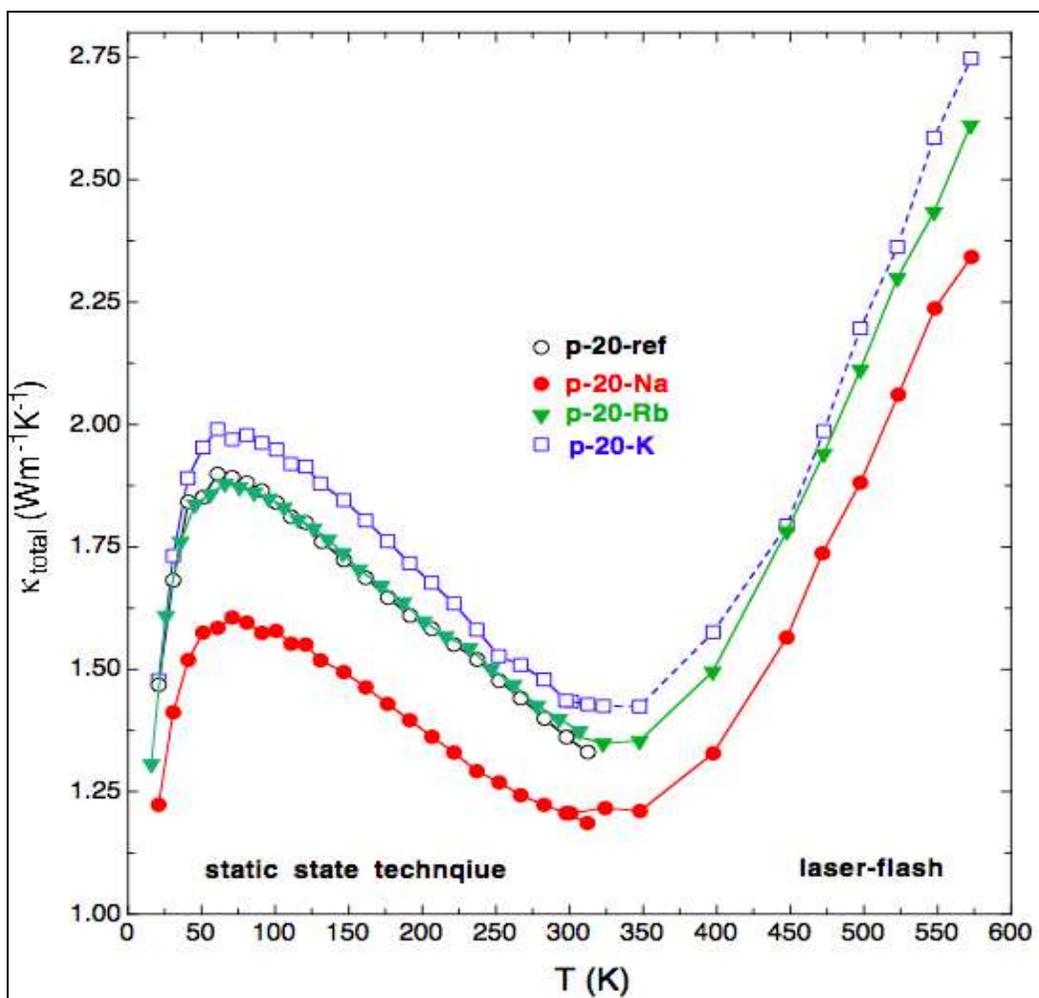


Figure 26. Laser Flash and Low Temperature Thermal Conductivity comparison of the thermal conductivity of Bi_2Te_3 measured along the same axis⁶

Differential Scanning Calorimeter

Experimental Procedure

Background

The 404 C Pegasus® Differential Scanning Calorimeter, DSC, is another instrument produced by Netzsch that directly affects the outcome of the Laser Flash. It accurately measures the heat flow rate to a sample and compares the rate to a reference material using the Ratio Method. As a result the specific heat of the sample is calculated. This procedure is beneficial when running the Laser Flash because their computer interfaces directly connect in order to transfer specific heat data and calculate the thermal conductivity of a sample. It is also beneficial because the DSC measures the stability of the material and can determine the temperature range the Laser Flash should safely be run at.

To find the specific heat of a sample three runs must be completed. The first run is a baseline and is used as a correction to the following two runs. The second run is the reference material. Sapphire, the reference material, is a stable material up to the high temperatures of the DSC. It is used as the reference material due to the fact that its specific heat data is programmed into the PC. The third run is the unknown sample. The three runs must begin at the sample temperature and have the same heating rate. This is necessary for the comparison of the sample and sapphire through the Proteus Analysis program.

Once the three runs are complete the Proteus Analysis program is opened and the three runs are compared through the Ratio Method. The Ratio Method compares the specific heat, C_p , of the sapphire to the specific heat of the sample with the following equations.

$$\text{Heat Flow} = \frac{Q}{\Delta t} \quad (20)$$

$$C_p = \frac{\text{Heat Flow}}{\text{Heat Rate}} \quad (21)$$

$$\text{Ratio} = \frac{DSC_{\text{Sample}} - DSC_{\text{Baseline}}}{DSC_{\text{Sapphire}} - DSC_{\text{Baseline}}} \quad (22)$$

$$\text{Ratio} \times C_p^{\text{Sapphire}} = C_p^{\text{Sample}} \quad (23)$$

Where Q is the heat flow and Δt is the change in time.

To find the stability of a sample only one run needs to be made. This run should be at an accelerated heating rate, allowing the melting or phase transition to be more evident. If the sample is not stable past a certain temperature it should be considered when running the Laser Flash.

Experimental Apparatus

The DSC consists of a 404 C Pegasus system (figure 27) that houses an S type thermocouple in an automated furnace. This thermocouple has a crucible holder that holds two crucibles at its junction. One crucible is always vacant, while the other is used to measure the baseline, sapphire, and sample.

When measuring a baseline or sample the system is first vacuumed and then purged with Argon gas at 50mL/min. This is completed twice to insure the absence of air from the system. After the second purge the valve is opened to let Argon continuously flow through the system during the run. The parameters are then set in the data acquisition program. These parameters include the sample mass, the heating rate, and the beginning and

ending temperatures. Once the system is purged for the last time and the parameters are entered the system is ready to run.

The furnace rises in temperature at the entered rate and as a result heats the sample. The thermocouple measures the temperature of the crucible at a certain time as well as the change in heat of the sample. With this information a DSC vs. time or temperature graph is created. Once the baseline, sapphire, and sample are measured under the same conditions the Ratio Method is applied and the sample's specific heat is determined.

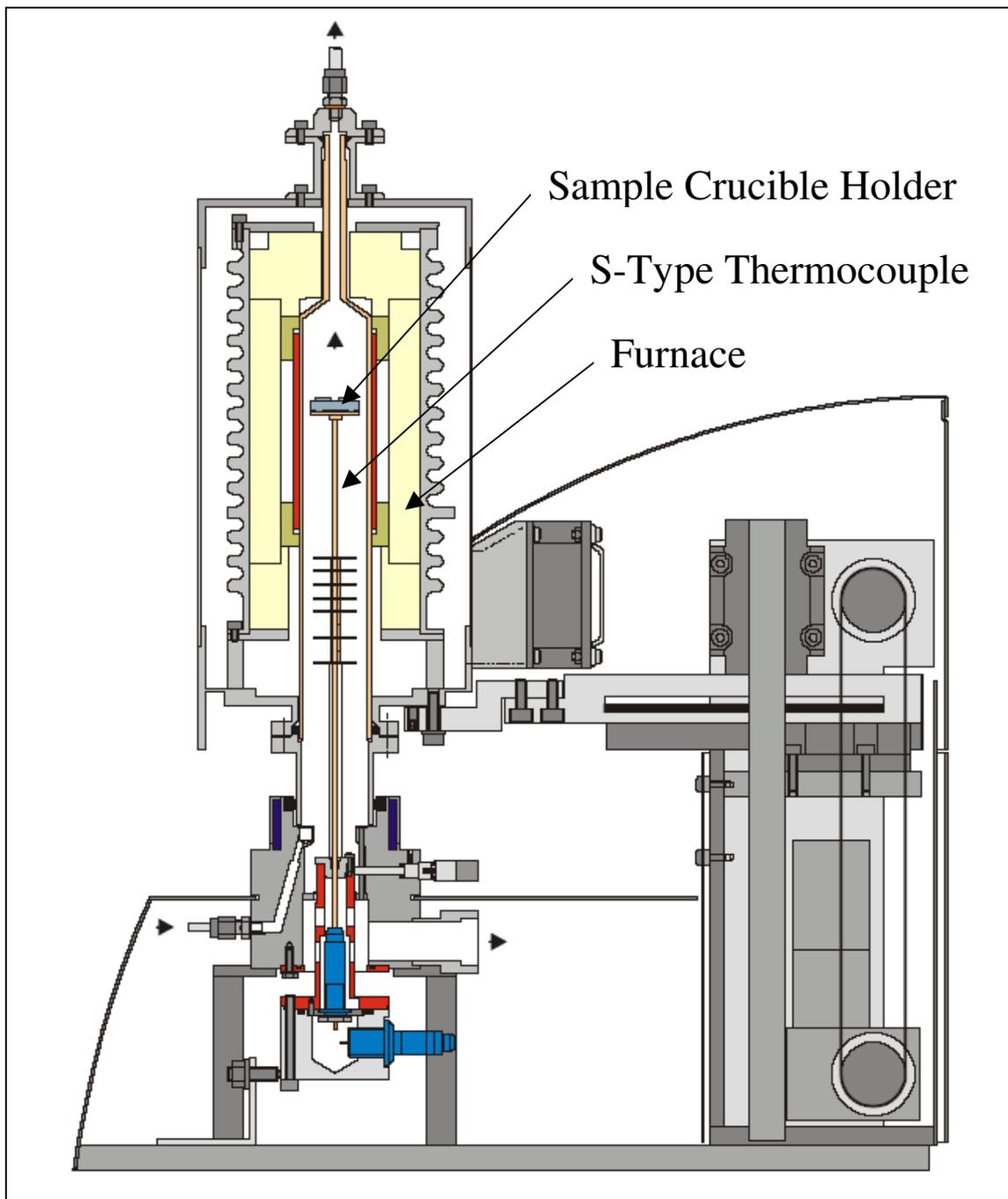


Figure 27. Netzsch Pegasus 404C® DSC⁶

Sample Mounting

The samples are run in a small platinum crucible lined with Aluminum Oxide, Al_2O_3 . The platinum is useful because it has a high thermal conductivity, while the Al_2O_3 is durable up to high temperatures and will not react with the measured material. These crucibles are cylindrical. They are about 5mm in diameter and 2mm deep. The system can measure both solids and liquids. However, due to the inexperience of the users the recommended sample is a solid sample about 4mm in diameter and 1mm thick.

The sample should be as flat on one side as possible. To ensure this the sample is roughly polished until the sample is guaranteed to sit flush with the crucible. The importance of this will be described in the results section.

Experimental Results

When measuring a sample with low thermal conductivity many ideas must be considered before running the sample such as the heating rate, sample mass, and sample to crucible contact. By not considering these factors the specific heat can be off by 5% depending on the sample. The importance of each factor can be found using equation 21

$$C_p = \frac{\text{Heat Flow}}{\text{Heating Rate}}$$
$$C_p = \frac{\frac{Q}{\Delta t}}{\text{Heating Rate}} \quad (24)$$

Where Q is the heat and t is the time. The heat is equal to the specific heat times the mass times the change in temperature (equation 22).

$$Q = C_p m \Delta T \quad (25)$$

As a result the heating rate, sample mass, and sample to crucible contact are important factors to attend to before measuring a sample on the DSC.

The DSC can measure a sample between 0.1 and 50 K/min. Because there is an abundance of samples that need to be measured, the faster the sample can be done the better. However, most of the samples that are run in the CAML laboratory have low thermal conductivity, which forces the sample to be run at a low heating rate. To optimize this rate different runs were completed on the same sample, Cadmium Rhenium Oxygen ($\text{Cd}_2\text{Re}_2\text{O}_7$), as seen in figure 28. The data was then compared to a measurement made on the PPMS system (Figure 29). The best run was completed with a heating rate of 5K/min. As a result finding the specific heat of one sample takes about two days.

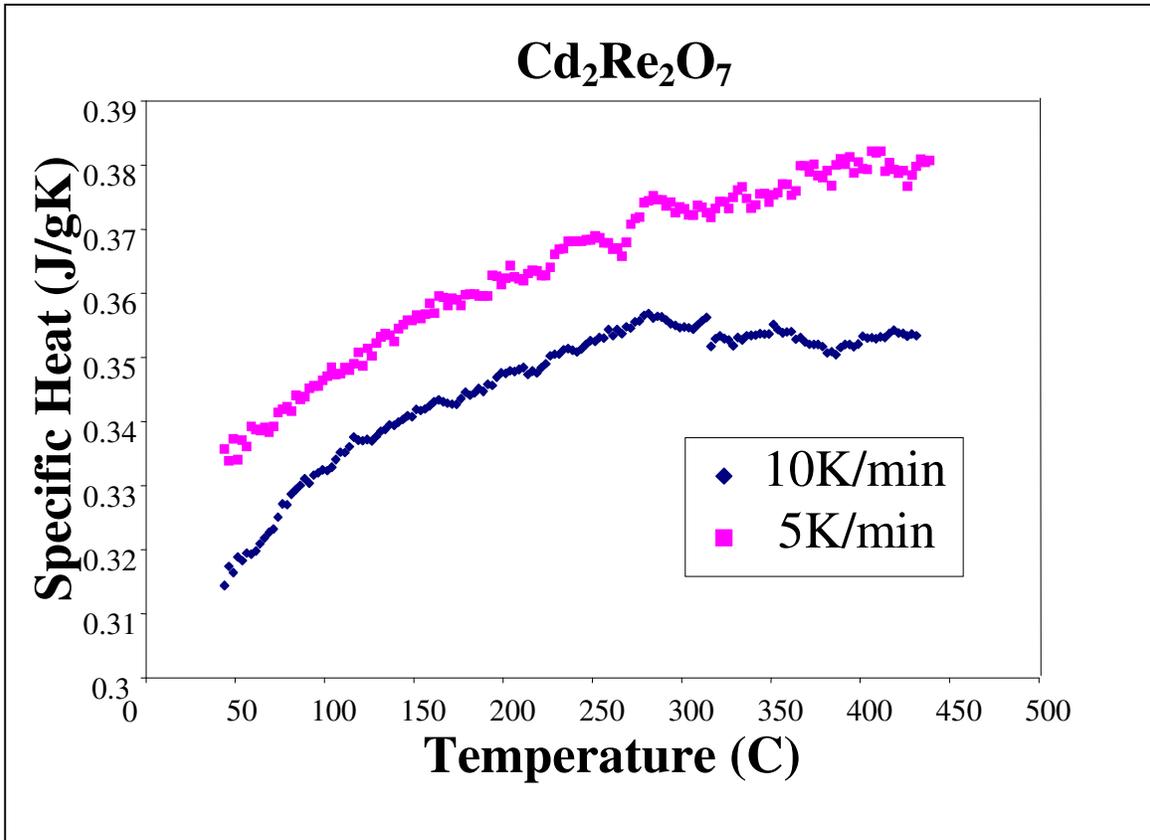


Figure 28. Specific Heat comparison of heating rates

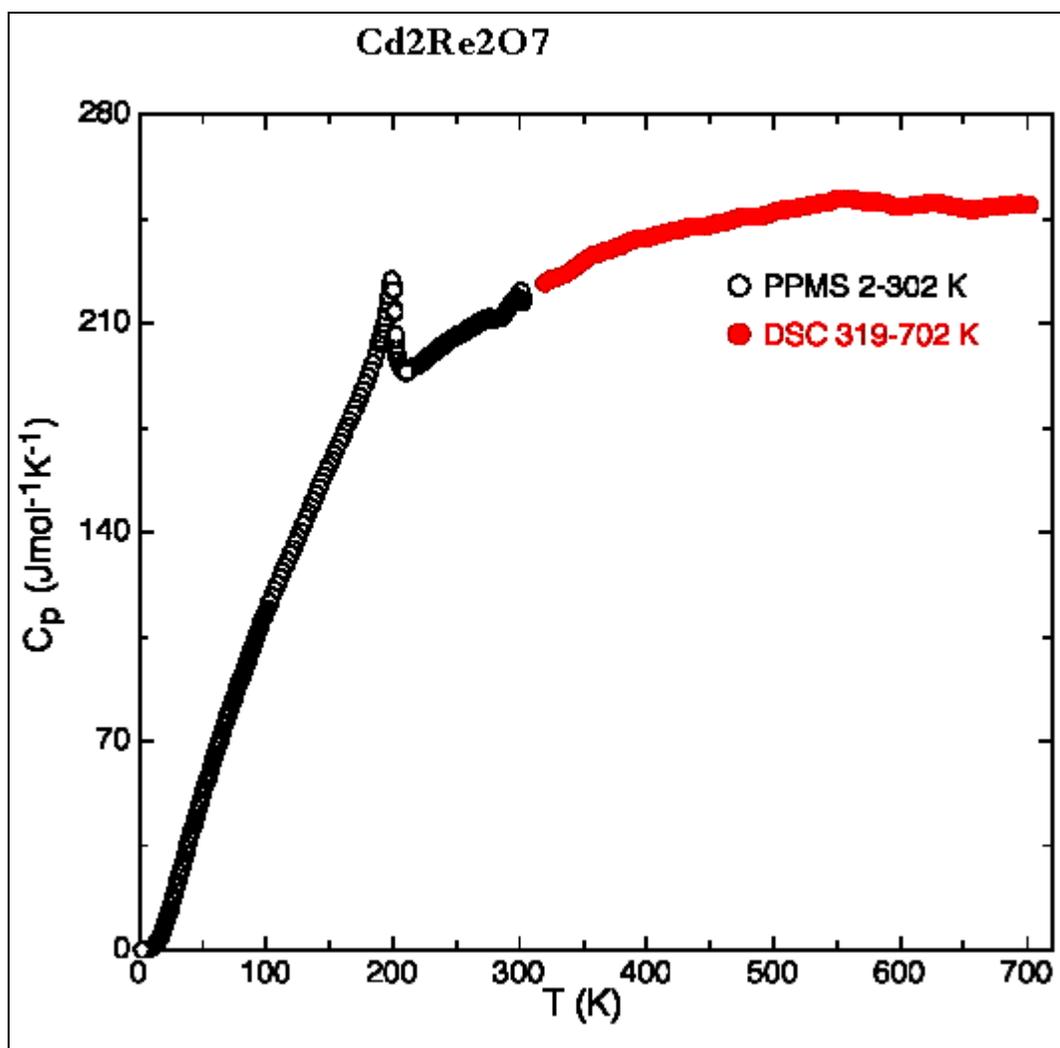


Figure 29. PPMS and DSC specific heat comparison⁷

Another factor that determines the accuracy of the DSC measurement is the mass of the sample. If the sample has low thermal conductivity the larger the mass of the sample the better the DSC run will be. Although the DSC can measure sample sizes ranging from 5mg to 100mg the optimum weight is determined by the density of the sample.

The crucible contact is the most important factor when measuring a sample with the DSC. If the sample is in good contact with the crucible the heating rate does not have to be as low as 5K/min. This is seen because of the fact that as the crucible bottom is heated the sample surface in contact with the crucible is heated at the same rate because of the platinum shell of the crucible. If only a small part of a low thermal conductivity sample touches the crucible the entire sample will not feel a change in heat. However, if the sample has a large, flat surface that remains in contact with the crucible bottom the sample will heat more rapidly, which allows for the increase in heating rate.

In conclusion for a good DSC measurement you need a large sample with a flat surface. If the sample does not have a very flat surface the heating rate should be lowered. However, it is more important to have a good surface to crucible contact than have a large sample. As a result the sample should always be polished before being run in the DSC.

Another use for the DSC is the measurement of sample stability. In a sample of normal thermal conductivity the sample stability is best measured at a heating rate of 20K/min. This allows the phase transition or melting point to be a more drastic change in slope as seen in figure 30 the melting of Gold.

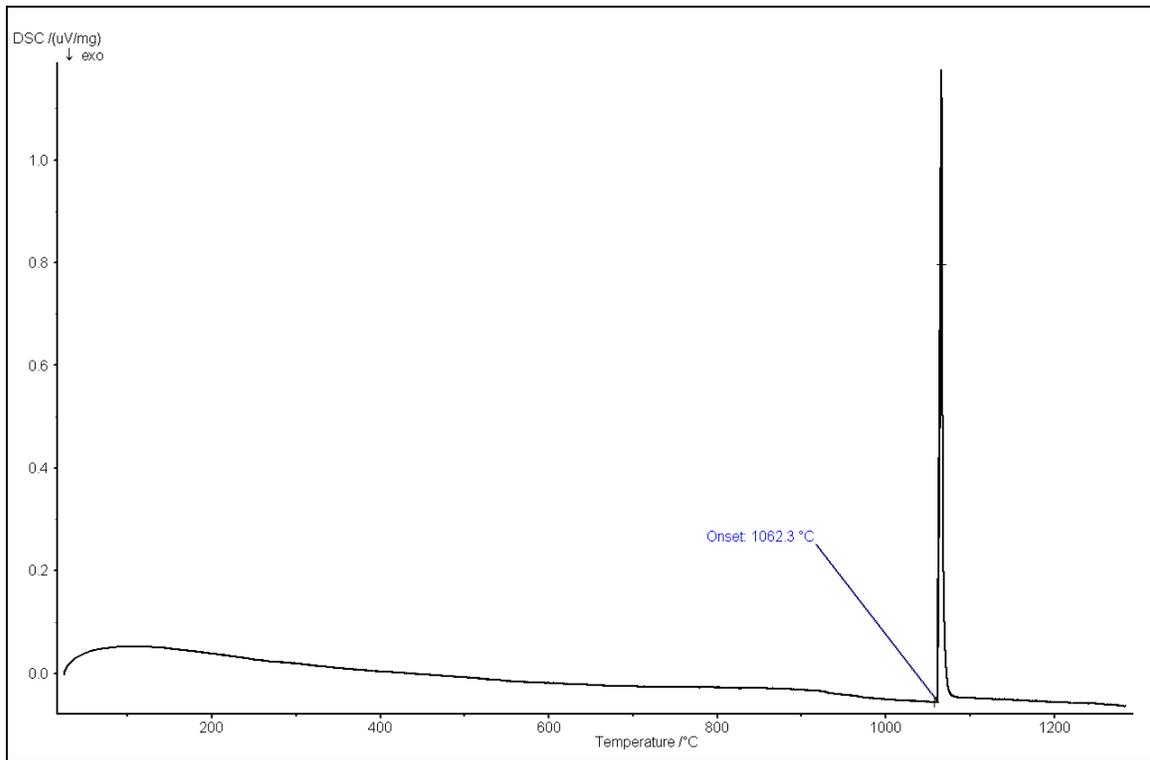


Figure 30. Melting point of Gold

CHAPTER FOUR COMPARISON

The low temperature thermal conductivity, TC, systems and the laser Flash have many advantages. The TC system measures the thermal conductivity between 15K to room temperature, while the Laser Flash measures thermal conductivity between room temperature and 1370K. The TC system also measures samples under a pressure of $1e^{-6}$ torr. This is advantageous because it prevents convection. The Laser Flash does not need to run under vacuum because convection loss will not drastically affect the measurement.

Although the TC and Laser Flash systems have many advantages they also have many disadvantages. As previously stated, the accuracy of both systems is between 5 and 15%. This can be overcome by an accurate dimension measurement. Another disadvantage of the TC system is the difficulty in mounting the samples. There is a large learning curve when mounting a sample to run on the TC systems from making the thermocouples to decreasing the amount of solder on the sample. However, with practice the mounting process is achievable. Another disadvantage of both systems is the sample size. As previously mentioned the sample size for the Laser Flash is between 8mm square and 25.4mm in diameter and about 2mm thick. Making a sample this large is difficult for a small lab. The TC system measures samples around 2x2x8mm, which is not as difficult to make but not necessarily the best measurements for decreasing radiation loss.

Although each system has its own advantages and disadvantages when measuring thermal conductivity, the biggest advantage of having more than one thermal conductivity system is the freedom to check the other systems. When measuring a sample on the low temperature thermal conductivity systems the sample is usually measured two to three times

on different systems. This insures the accuracy of the measurement. However, there is only one Laser Flash, and although a sample can be run two or three times on the same system it does not guarantee that the sample run is accurate. As a result many samples are measured on the Laser Flash as well as the low temperature thermal conductivity systems. This guarantees that the data is both accurate and reproducible. A comparison between the two systems can be seen in figure 31.

HfZrNiSnSb Thermal Conductivity Comparison

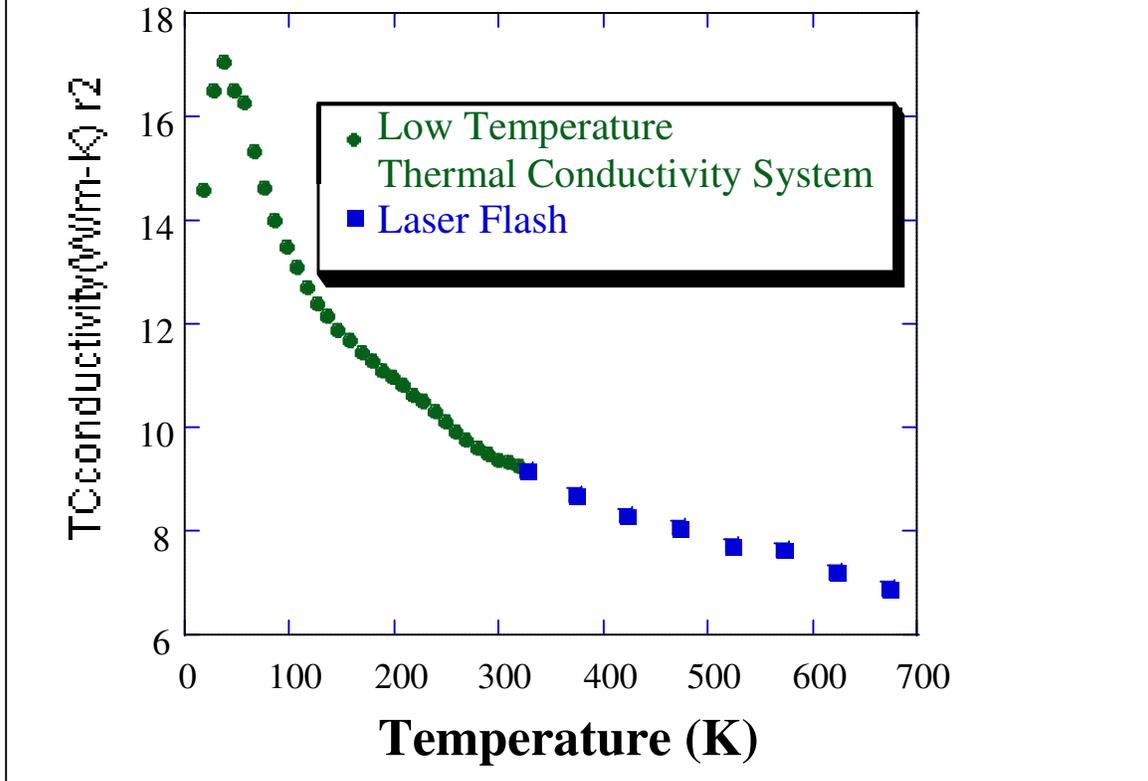


Figure 31. Low Temperature and High Temperature Thermal Conductivity comparison

APPENDICES

A:

Procedure list for mounting Low Temperature Thermal Conductivity measurements

- 1.) Cut 2 #38 Copper wires as long as the thickness of the sample.
- 2.) Scrape off insulation of one side of the wires.
- 3.) Coat insulated side of wire in stycast.
- 4.) Place one wire stycasted side down about 2mm from the top of the sample.
- 5.) Place the other wire stycasted side down about 4mm from the top of the sample.
- 6.) Let Stycast dry for 12 to 24 hours.
- 7.) Measure the width and thickness of the sample.
- 8.) Measure the distance between the Copper wires.
- 9.) Unscrew Copper heat sink from the sample puck.
- 10.) Solder sample into depression of the heat sink using Lead Tin (PbSn) solder.
- 11.) Once cooled, screw heat sink back onto the puck assuring the stycasted side points away from the middle of the puck.
- 12.) Attach a 0.001in. diameter Constantan Chromega thermocouple to the specified pads on the puck using PbSn solder.
- 13.) Attach the junctions of the thermocouple to the Copper wire using PbSn solder.
- 14.) Secure a 120 ohm strain gauge resistive heat to the top, center of the sample using 5 Minute Epoxy.
- 15.) Once dry cut two Phosphor Bronze (PBz) wires about 6mm in length and scrape 1mm of insulation off each end.
- 16.) Do the same to the end of the heater wires.
- 17.) Solder one end of the PBz to one end of the heater wire using PbSn solder.
- 18.) Do the same to the other PBz wire and the other end of the heater wire.
- 19.) Once cooled coat the junctions created in step 15 and 16 with nail polish to reinsulate the wires.
- 20.) Using PbSn solder attach the other ends of the PBz wires to their specified pads and pins on the puck.
- 21.) Repeat for another sample on the other side of the puck.

B:

Procedure list for preparing Laser Flash thermal diffusivity measurements

- 1.) Measure the diameter (or width and length) and thickness of the sample.
- 2.) Calculate the volume of the sample ($\pi \cdot h \cdot r^2$ or $l \cdot w \cdot t$).
- 3.) Weigh the sample.
- 4.) Calculate the density of the sample (m/V).
- 5.) Coat one side of the sample with graphite using graphite spray.
- 6.) Repeat until there is no reflectivity.
- 7.) Repeat to the other side of the sample.
- 8.) Place sample in the puck that is the right size and cover with a lid.

C:

Procedure list for preparing DSC measurements

- 1.) Make sure sample fits in the Aluminum Oxide coated Platinum crucible.
- 2.) Polish one side of the sample using sand paper, Dremel tool, or file until completely flat.
- 3.) Weigh sample
- 4.) Place sample in crucible with the flat side down.
- 5.) Place Platinum lid on the crucible.

D:

Flow chart for running the Low Temperature Thermal Conductivity system

- 1.) Make sure water in and return is open to the system
- 2.) Place puck with samples mounted into cryocooler head
- 3.) Replace all radiation shields
- 4.) Check system components
- 5.) Thermocouple = $50-70\Omega$
 - 5a.) Thermocouple $\neq 50-70\Omega$
 - 5b.) Remount sample and begin at 1
- 6.) Heater = 120Ω
 - 6a.) Heater $\neq 120\Omega$
 - 6b.) Remount sample and begin at 1
- 7.) Turn on vane pump
- 8.) Once pump is around 5mTorr turn on turbo pump
- 9.) Open Labview for thermal conductivity
- 10.) Enter desired information
- 11.) Run samples

E:

Flow chart for running Laser Flash

- 1.) Turn on system
- 2.) Check if there is enough cooling water
- 3.) Enough Water
- 3a.) Not enough water
- 3b.) Fill with distilled water until full
- 4.) Fill dewar with liquid Nitrogen
- 5.) Lower furnace and clean the radiation shields with alcohol covered swab
- 6.) Place sample, sample holder, and lid into designated sample carrier
- 7.) Three samples
- 7a.) One or two samples
- 7b.) Cover empty sample carrier holes with special lid
- 8.) Raise furnace
- 9.) Close valve to system
- 10.) Vacuum for three minutes
- 11.) Purge until pressure is greater than 0
- 12.) Vacuum for three minutes
- 13.) Purge until pressure is greater than 0
- 14.) Open valve
- 15.) Adjust purge rate to 75mL/min
- 16.) Open LFA measurement on PC
- 17.) Enter desired information
- 18.) Run samples

F:

Flow chart for running DSC

- 1.) Turn on the system
- 2.) Raise Furnace
- 3.) Place empty crucible and lid in system
- 4.) Lower Furnace
- 5.) Close valve to system
- 6.) Vacuum for three minutes
- 7.) Purge until pressure is great than 0
- 8.) Vacuum system for three minutes
- 9.) Purge until pressure is greater than 0
- 10.) Open valve to system
- 11.) Adjust purge rate to 50mL/min
- 12.) Open DSC measurement on PC
- 13.) Enter desired information
- 14.) Run baseline
- 15.) Raise Furnace
- 16.) Place Sapphire in crucible and replace lid
- 17.) Lower Furnace
- 18.) Close valve to system
- 19.) Vacuum for three minutes
- 20.) Purge until pressure is greater than 0
- 21.) Vacuum system for three minutes
- 22.) Purge until pressure is greater than 0
- 23.) Open valve to system
- 24.) Adjust purge rate to 50mL/min
- 25.) Open DSC measurement on PC
- 26.) Enter desired information
- 27.) Run standard
- 28.) Raise Furnace
- 29.) Remove Sapphire from crucible
- 30.) Place prepared sample into crucible
- 31.) Replace lid
- 32.) Lower Furnace
- 33.) Close valve to system
- 34.) Vacuum for three minutes
- 35.) Purge until pressure is great than 0
- 36.) Vacuum system for three minutes
- 37.) Purge until pressure is greater than 0
- 38.) Open valve to system
- 39.) Adjust purge rate to 50mL/min
- 40.) Open DSC measurement on PC
- 41.) Enter desired information
- 42.) Run sample

- 43.) Run DSC analysis program
- 44.) Open baseline, Sapphire, and sample run
- 45.) Open ratio method
- 46.) Save specific heat data

G:

Advantages and disadvantages of the Low Temperature Thermal Conductivity system

Advantages	Disadvantages
Measures TC from 15 to 300K	Accuracy $\pm 10\%$
Pressure $1e-6$ torr	Degree of Skill
Steady state method	1 run takes 18-30 hours
System Check	Sample size $2 \times 2 \times 8$ mm
Preparation	
1 run takes 18-30 hours	

H:

Advantages and disadvantages of the Laser Flash system

Advantages	Disadvantages
Measures TC from 300K to 1370K	Accuracy $\pm 10\%$
Measures 3 samples in about 24 hours	DSC measurement
	Sample Size 8x8, 10x10, 10, 12.7, 25.4 mm
	Sample orientation

I:

List of considerations before running a sample

- 1.) Are we interested in the low and high temperature thermal conductivity?
 - a.) Is the sample anisotropic?
 - b.) Can the sample be altered to measure the same direction on the low temperature thermal conductivity and laser flash systems?
- 2.) What temperature should the laser flash be run to?
 - a.) What is the melting point?
 - b.) Are there any phase transitions?

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