TRANSPORT PROPERTIES OF 40% LA FILLED SKUTTERUDITE THIN FILMS -
THEORY AND INSTRUMENTATION

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ABSTRACT

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This study researches thin films fabricated by pulsed laser ablation on tempered glass substrates using 40% La filled-Skutterudite. In general, laser ablated films exhibit up to 70% amorphous structure and vary in thickness by about 20% from center to edge. The thermoelectric figure of merit determined using a modified version of the Harman\textsuperscript{1} equation at room temperature approaches a value of 18. The modifications include the effects of the substrate and its thickness. An empirical figure of merit \( ZT = \frac{\delta V_{ad}}{\delta V_{iso}} - 1 \) obtained using the voltage measurements under adiabatic and isothermal conditions was extrapolated to zero substrate thickness. A total of 16 samples were prepared in three ablation runs with different substrate thickness and with an average film thickness of 95 nm. The higher figure of merit obtained compared to bulk samples can be the result of a variety of possibilities: enhanced Seebeck coefficient and size limited thermal conductivity in both electronic and lattice components due to limited mean free path.
Dedication

I dedicate this thesis to my loving wife, Dilu, who did more than her share around the house as I sat at the computer and for her motivation and support throughout the course of the thesis. This thesis is also dedicated to my parents, who gave me unconditional love and support throughout my life.
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CHAPTER 1
THEORY AND INTRODUCTION

1.1 Introduction

Thermoelectricity is of great scientific and technological interest due to the possibility of harvesting wasted heat in almost all power generating applications. Recent developments in theoretical studies on thermoelectricity, as well as newly discovered thermoelectric materials, provide new opportunities for a wide range of applications. Thermoelectric devices are based on the fact that when certain materials are heated, they generate a significant electrical voltage. Conversely, when a current is applied, they transport heat as well and become hotter on one side and colder on the other. These are the key factors that enter into the applications of thermoelectric materials. Novel thermoelectric materials have already resulted in new consumer products. One of the very important applications is the utilization of thermoelectric materials to produce electricity in spaceships that travel far from the sun, where it is difficult to obtain solar power. Thermoelectric generators for space carry radioactive materials. Electric power is obtained when the heat is converted into electricity using efficient thermoelectric materials.

As mentioned, thermoelectricity is the conversion of heat directly into electrical energy and vice versa. It involves an electron transport property that combines thermal and electrical effects. It comprises three major effects: the Seebeck effect, the Peltier effect, and the Thompson effect. In a conductor there is always a balance between these effects. A constant heat current flow in a conductor creates a constant temperature gradient. As a result a thermoelectric voltage develops, or, what is equivalent, a constant electric field develops between the hot end and the cold end. This phenomenon is known as the Seebeck effect and the Seebeck coefficient $S$ is operationally defined as the ratio of the voltage difference $\Delta V$...
to the temperature difference $\Delta T$ between the two junctions with zero electric current

$$S = \frac{\Delta V}{\Delta T}$$  \hfill (1.1)

The Seebeck coefficient is not necessarily a linear function of temperature. It depends on the absolute temperature, electronic structure, and material properties of the conductor. However, it remains fairly constant over small temperature ranges. The Peltier effect is inversely related to the Seebeck effect; it is the generation of a heat flow between the two ends of a conductor due to an applied current. The Peltier coefficient is a measure of heat current carried per unit charge through a conductor. These two effects are the most basic out of the three effects and may also be called the Peltier-Seebeck effect instead of the thermoelectric effect. The Peltier coefficient is defined as the ratio of the thermal current to electrical current passing along a conductor.

The Seebeck effect is illustrated in Figure 1.1, where a junction couple is comprised of a p-type and n-type semiconductor connected in series electrically and in parallel thermally. An e.m.f. is generated proportional to the temperature gradient between the hot and cold junctions. Figure 1.2 indicates the inverse Peltier effect. The same setup connected to a power supply results in one end absorbing heat and the other giving off heat because of the heat flow from one junction to the other. The cooling effect is proportional to the applied current.

These coefficients are related by the first Thompson relation, also known as the Kelvin relation, that is obtained from thermodynamic considerations

$$\Pi = ST$$  \hfill (1.2)

where $\Pi$ is the Peltier coefficient, $S$ is the Seebeck coefficient, and $T$ is the absolute temperature.
A common practical application of these effects is the thermocouple. Figure 1.3 shows a couple of junctions between two dissimilar conductors A and B, that are connected in a complete circuit. A thermocouple is commonly used to measure a temperature difference or to measure absolute temperature if one end is fixed at a known temperature.
If \( S_A \) and \( S_B \) are the respective Seebeck coefficients of the two conductors, and \( T_1 \) and \( T_2 \) are the respective temperatures at junction 1 and 2, then the voltage developed due to the temperature difference can be derived from

\[
V = (S_B - S_A) \times (T_2 - T_1) \tag{1.3}
\]
There are two major transport mechanisms that contribute when a temperature difference appears along a conductor. The first is electron or charge carrier diffusion. Depending on the temperature gradient present in a metal, alloy, or semiconductor, electrons at the hotter end are more active or energetic compared to those at the cooler end. Thus they are more likely to travel longer distances. Hence, as a result an electric field is generated inside the conductor. The other mechanism is phonon drag, which is caused by the net phonon flux from the hotter end to the cooler end of the conductor, “dragging” electrons along due to electron-phonon collisions.

1.2 Thermoelectric Figure of Merit

The Thermoelectric Figure of Merit (FOM) or the thermoelectric Coefficient of Performance (COP) is a direct indicator of a particular material’s efficiency at converting heat into
electricity or vice versa. It is defined as the ratio of the power applied to the sample to the rate of heat conducted through the sample.

\[ Z = \frac{P}{QT} \]  

(1.4)

where \( P \) is the power applied to the sample, \( \dot{Q} \) is the rate of heat flow through the sample, and \( T \) is the absolute temperature. By using standard formulas for \( P \) and \( \dot{Q} \), and with some rearrangements the coefficient of performance can be obtained as

\[ Z = \frac{\sigma S^2}{\kappa} \]  

(1.5)

where \( \sigma \) is the electrical conductivity, \( \kappa \) is the thermal conductivity, and \( S \) is the Seebeck coefficient with units usually in V/K. Therefore \( Z \) has units of inverse temperature. If the average temperature \( \bar{T} \) of the sample is multiplied by \( Z \), then a dimensionless thermoelectric figure of merit \( ZT \) can be obtained.

\[ ZT = \frac{\sigma S^2 \bar{T}}{\kappa} \]  

(1.6)

The quantity \( ZT \) is the most commonly used because it is a dimensionless measure of the thermoelectric efficiency of the material. As such, it is a better way of comparing the potential efficiency of two different materials. If we replace the electrical conductivity by electrical resistivity, \( ZT \) can be expressed as

\[ ZT = \frac{S^2 \bar{T}}{\rho \kappa} \]  

(1.7)

From the definition of \( ZT \), if we limit our investigation to a fixed temperature, then there are several ways that the efficiency can be increased. This can be accomplished by increasing the Seebeck coefficient, decreasing the thermal conductivity or the electrical resistivity of the material, or by any combination of these changes.
In our exploration, the focus was to reduce the thermal conductivity of the sample, which is a combination of the lattice thermal conductivity and the carrier thermal conductivity. A compound of 40% La filled Skutterudite been shown to have minimal lattice thermal conductivity over the entire range of La concentration in bulk form. Additionally, thin films with thickness less than the thermal mean free path of the carriers can decrease the thermal conductivity by lowering the mean free path. Another way to reduce lattice conduction is to fabricate an amorphous sample. All of these considerations were part of the design of this experiment using laser ablated thin film samples.

1.3 Skutterudite

Skutterudite is a mineral of the form TX, where T is a transition metal like Co, Fe, or Ni, and X could be a pnictogen atom like P, As, or Sb. The crystal structure of Skutterudite is shown in Figure 1.4. Skutterudite has the potential to be a very good thermoelectric material due to the open nature of its crystal structure and its ability to accommodate heavy elements with smaller diameter, such as lanthanum, cerium, and ytterbium (Rare Earths). Figure 1.5 shows a Skutterudite structure with filling ions. The material used in this study is filled with lanthanum (La) in 40% of its voids. The filler atoms are loosely bound in the voids and can rattle around their equilibrium position. As a result, the (lattice) thermal conductivity is reduced by them vibrating and absorbing heat-carrying phonons. The doping process affects all the electronic (carrier) transport properties so that they can be optimized in accord with desired goals. As a result of its special features, it has become popular as a high efficiency thermoelectric material.

1.4 Goals of the Project

By measuring the thermoelectric coefficient of performance of thin Skutterudite films using a modified version of Harman’s method, our ultimate goal is to obtain a thermoelectric
Figure 1.4: Skutterudite Structure with Voids

Figure 1.5: Filled Skutterudite Structure
material with a higher efficiency in converting heat into electricity than has been reported
to date. Most of the experiments in the recent past have been carried out on bulk crystalline
Skutterudite. To our knowledge there are no reports concerning the properties of amorphous
thin films made of this material. It is vital to consider the effects of the substrate on the
apparent or “experimental” thermoelectric FOM of the Skutterudite film and how it can be
used to interpret the results. The substrate also conducts heat and in a simple model we
take the amount of heat flow to be directly proportional to the thickness of the substrate.

The entire investigation was conducted to attempt to discover the dependence of the
experimentally determined apparent thermoelectric figure of merit for Skutterudite on the
substrate thickness, and thus to evaluate the feasibility of utilizing thin films for practical
applications.

1.5 Probable Applications

A thin film of an efficient thermoelectric material is a great prospect to manufacture
superior thermoelectric devices, since they have a wide range of applications. Instead of
producing the Skutterudite thin film on a glass substrate, it could be formed under a solar
panel. In that way the thermoelectric material would collect the heat energy rejected by
the solar panel, even as the solar cells convert solar radiation into electrical energy. This
arrangement would help increase the practical efficiency (which is now in the range of 10%-
12%) of a solar cell by converting both heat and light into electricity.

Another potential application would be in an automobile where the wasted heat can
be converted into electricity and reused. If a thin film of thermoelectric material can be
produced on a flexible substrate, such as a polymer, then by winding it around the exhaust,
the waste heat can be captured. Using this technique, it is also possible to harvest most
of the waste heat generated at different industrial sites around the world, thus decreasing
thermal pollution and the need for more energy. However, many researchers feel they are far
from being able to adequately extract electricity directly from heat sources. Thermoelectric materials will first appear in specialty applications. If efficiencies can be further increased however, then whole other areas of technology will be able to bring the idea of harvesting heat into play. Discovering the most efficient thermoelectric material is an important step on the way to this goal.
2.1 Preparation of the Sample

Tempered glass plates of 2.5 cm by 2.5 cm, typically used by the biologist as a microscope cover slide, were used as the substrate material for the thin films. First, they were cleaned with distilled water and then with isopropyl alcohol. The thickness of the substrate was varied by gluing (with a glue that had a higher thermal conductance compared to tempered glass) two or more glass plates together. Assuming that the result would give a homogeneous set of samples, a set of 4 substrates were carefully mounted onto the sample holder as shown in Figure 2.1 inside the vacuum chamber. The thin films were fabricated by laser ablation using 40% La filled Skutterudite La$_{0.4}$(Fe$_3$Co)Sb$_{12}$ as the target material. The substrates were ablated for 24 minutes in order to get the required thickness of Skutterudite on the plates. A Nd:YAG laser with CW power of 700 mW, 6 ns pulses, and a 10 Hz repetition rate was used as the beam and ablated the target material which was set at an angle of 45° with respect to the beam (Figure 2.2). The ablation vacuum was brought down to a pressure of $1.5 \times 10^{-6}$ Torr using an ion diffusion pump, turbo-molecular pump, and a roughing pump. The samples were carefully removed from the chamber and stored in a refrigerator to avoid contamination and oxidation of the films. Three sets of samples, each of which contained four samples with different substrate thickness, were fabricated. Altogether 12 thin film samples were produced.
Figure 2.1: Four Samples Mounted on the Sample Holder

Figure 2.2: Schematic Diagram of the Laser Ablation Setup
2.2 Wiring and Mounting the Sample

Figure 2.3 shows a schematic diagram of the sample. Manganin wires of 20 cm in length were stripped at both ends using StripX® to remove the insulation coating. The stripped wires were connected to the thin film using highly conductive silver paint to ensure good contact. After complete drying of the silver paint, the contacts were checked for proper connection using an ohmmeter. As Figure 2.3 shows, two silver paint stripes were made for the current probes (input signal) to make the current and heat flow uniform through the sample. Two voltage probes were fused to the sample at a distance of 1 cm with a silver paint dot. The sample was carefully placed on a grease-coated Teflon block inside the vacuum can as shown in Figure 2.4, and the connections were tinned for better connectivity. Finally, all the connections were tested using an ohmmeter before sealing the vacuum can.

![Figure 2.3: Schematic Diagram of the Wired Sample](image-url)
2.3 Vacuum System and Pumping

The vacuum can or chamber was sealed using an indium O-ring. An O-ring is placed into the groove between the housing and the can, then both units are tightened together using 12 screws around the can. The screws were tightened in such a way that a constant pressure was applied to the indium O-ring. As a result the indium spreads evenly, creating a good vacuum seal.

The vacuum system is comprised of an oil diffusion pump and a mechanical pump as shown in Figure 2.5. The mechanical pump was used for rough pumping for the initial 24 to 36 hours leaving valve 1 completely open. After the pressure of the vacuum can stabilized,
the oil diffusion pump was turned on. Then valve 1 was closed and valve 3 was opened. The diffusion pump was allowed to warm up for 30-45 minutes and valve 2 was opened to do the rest of the pumping of the system. By means of proper sealing at the vacuum can the pumping system was able to achieve a pressure of $2 \times 10^{-4}$ Torr on average.

![Figure 2.5: Schematic Diagram of the Vacuum System](image)

2.4 Experimental Apparatus and Data Collection

Figure 2.6 shows a schematic diagram of the experimental setup. After mounting the sample, the system was brought to the required pressure. The circuit was driven with a square wave voltage of 100 Hz from a TENMA® model:72-380 function generator which applied to a standard resistor of 10 Ohms in series with the sample. The input current was kept very low in order to avoid Joule heating. Further, the input signal was verified and recorded by using channel 1 of a Tektronix® model:2213 analog oscilloscope. Next,
the output of the circuit was connected to channel 2 of the analog oscilloscope and to the
digital oscilloscope which was operated by the computer. The output was observed and
recorded in digital form on the computer using a PCI 5102 card by National Instruments,
which was interfaced with the LabVIEW® program. Necessary adjustments were made on
the computer to obtain the best waveform that would accurately produce the recorded data.
The best possible output was recorded for 60 runs, each of which contained 1000 voltage
data points plotted against the time. The same procedure was repeated for the remaining
11 thin film samples to obtain data.

2.5 Square Wave Input and Output

Thin film samples evolve with time. Thus, the samples have a tendency to oxidize and
change their original nature. Oxidation increases as the sample gets heated up. Therefore,
the current that drives the circuit was kept low; additionally, it flowed for a short period
of time. Hence, to ensure repeatability of the measurements within a short period of time
a square wave was used as the input. In addition, a square wave input would eliminate
the asymmetry of the sample. Even though the input current is very small, if we assume
there is significant Joule heating, then the direction of the heat gradient due to Joule heating
changes direction with the alternating current, thus balancing any thermal effects. Moreover,
the thermoelectric voltage decays rather slowly compared to the resistive voltage after the
current flow is changed. Therefore, rapid data collection is used to precisely separate the
thermoelectric and resistive voltages. Increasing the input signal frequency was limited due
the constraints of the measurement equipment. The equipment is more sensitive in and
around 100 Hz, limiting the experiment to operate in that frequency.
2.6 Signal Averaging

Signal averaging was done manually by extracting the voltage measurements for 60 trials for one sample to a single Microsoft Excel® work sheet. The readouts were averaged to reduce the noise by a factor of $\sqrt{60}$. The number of trials, 60, was selected because the averaged output of this number appears to reduce the noise sufficiently. Finally, the average voltage readings were plotted against time for further analysis. These plots were used to find the separate voltages under adiabatic and isothermal condition.

2.7 Modified Harman Equation

In order to properly analyze the thermoelectric FOM of Skutterudite thin films, modifications of the Harman equation are necessary. Alterations were made to include the effects of the thin film substrate.

The dimensionless thermoelectric figure of merit $ZT$ is

$$ZT = \frac{S^2T}{\rho k}$$ \hspace{1cm} (2.1)

Here the values $S$, $T$, and $\rho$ are considered to be constants for the material under study. However, there are two contributions to the thermal conductivity: electronic thermal conductivity $\kappa_e$ and lattice thermal conductivity $\kappa_l$

$$\kappa = \kappa_e + \kappa_l$$ \hspace{1cm} (2.2)

The contribution to the electronic thermal conductivity is reported to be minimal for 40% La-filling\(^5\). Therefore, we expect the total thermal conductivity of the material to be dominated by the lattice thermal conductivity.

$$\kappa \simeq \kappa_l$$ \hspace{1cm} (2.3)
2.7.1 Development of the Equation for the Experimental Thermoelectric FOM

If an electric current \( I \) is applied to the sample at absolute temperature \( T \), there arises a heat current due to the Peltier effect, and the rate of heat flow \( \dot{Q} \) can be expressed as

\[
\dot{Q} = \Pi I
\]  

(2.4)

where \( \Pi \) is the Peltier coefficient.

Thermodynamically, it is true that the Peltier and Seebeck coefficients are related by

\[
\Pi = ST
\]  

(2.5)

This gives

\[
\dot{Q} = SIT
\]  

(2.6)

A conduction heat current \( \dot{Q}_\kappa \) will flow through the sample to balance the Peltier heat current \( \dot{Q}_\Pi \) in order to maintain equilibrium. For the sample under consideration, if the temperature difference is \( \delta T \) over a distance \( \delta x \) with thermal conductivity \( \kappa \) and common cross sectional area \( A \), then the rate of conduction heat current can be expressed as

\[
\dot{Q}_\kappa = -\kappa A \frac{\delta T}{\delta x}
\]  

(2.7)

Equating 2.4, 2.5, and 2.6 for equilibrium in the steady state

\[
\dot{Q}_\Pi = \Pi I = SIT = \dot{Q}_\kappa = -\kappa A \frac{\delta T}{\delta x}
\]  

(2.8)

The steady state temperature difference across the sample is therefore:

\[
\delta T = \frac{S T I \delta x}{\kappa A}
\]  

(2.9)
Under adiabatic conditions the thermoelectric voltage $\delta V_{th}$ generated due to the temperature gradient $\delta T$ is

$$\delta V_{th} = S \delta T = \frac{S^2 T I \delta x}{\kappa A}$$  \hspace{1cm} (2.10)

The potential difference that is generated under isothermal condition is simply the voltage given by Ohms’ law

$$\delta V_{iso} = RI$$  \hspace{1cm} (2.11)

where $\delta V_{iso}$ is the isothermal voltage and R is the resistance of the sample. Substituting equation 2.10 in 2.9 gives

$$\delta V_{th} = \frac{S^2 T \delta V_{iso} \delta x}{\kappa R A} = \left( \frac{S^2 T}{\rho \kappa} \right) \delta V_{iso}$$  \hspace{1cm} (2.12)

Under adiabatic conditions the total potential difference $\delta V_{ad}$ across the thin film sample is the sum of both the thermoelectric voltage and the isothermal (Ohmic) voltage.

$$\delta V_{ad} = \delta V_{th} + \delta V_{iso} = \delta V_{iso} (1 + ZT)$$  \hspace{1cm} (2.13)

$$ZT = \frac{\delta V_{ad}}{\delta V_{iso}} - 1$$  \hspace{1cm} (2.14)

If there were no substrate, the experimental figure of merit could be determined by measuring both the adiabatic and isothermal voltages and by using the Harman equation (2.14) above.

The thin films used in this experiment were fabricated on tempered glass plates of thicknesses ranging from 0.145 mm to 0.58 mm. The presence of the substrate affects the derivation given above because part of the conduction heat flow is borne by the substrate itself. The values of $\delta V_{ad}$ and $\delta V_{iso}$ can still be used to obtain an empirical FOM value using the Harman equation, but the FOM of the film specimen can only be determined by extrapolating by varying the substrate thickness.
2.8 Adaptation for Thin Film with Substrate

As mentioned in section 2.7.1 the rate of heat flow through the sample in the steady state is considered. The conduction heat current flows along two parallel paths: through the thin film sample and through the glass substrate. The fraction of conduction heat current that flows through each portion depends on the thermal conductance of each part.

The rate of conduction heat flow $\dot{Q}_\kappa$ can therefore be expressed as

$$\dot{Q}_\kappa = \frac{\kappa_g A_g \delta T}{\delta x} + \frac{\kappa_s A_s \delta T}{\delta x}$$

where $\kappa_g$ is the thermal conductivity of the glass substrate, $\kappa_s$ is the thermal conductivity of the thin film, $A_s$ and $A_g$ are the respective cross sectional areas of the thin film and glass substrate, and the common temperature gradient is $\frac{\delta T}{\delta x}$.

We can write

$$\dot{Q}_\kappa = \frac{\kappa_g A_g \delta T}{\delta x} + \frac{\kappa_s A_s \delta T}{\delta x} = \Pi = SIT$$

If we substitute $A_g = wt_g$ and $A_s = wt_s$ in the above expression, we get

$$\delta T = \frac{SIT \delta x}{\kappa_s wt_s + \kappa_g wt_g}$$

where $w$ is the common width to the thin film and substrate, $t_g$ is the thickness of glass substrate, and $t_s$ is the thickness of the film.

Under adiabatic conditions the thermoelectric voltage is;

$$\delta V_{ad} = \frac{S^2 T \delta X \delta V_{iso}}{\left(\kappa_s + \kappa_g \frac{A_g}{A_s}\right) A_s R} + \delta V_{iso}$$

If we replace $\frac{\delta x}{A_s R}$ by $\frac{1}{\rho_s}$; that is the resistivity of the sample

$$\rho_s = \frac{A_s R}{\delta x}$$
We obtain a relationship between the empirical thermoelectric FOM and the ratio of voltages under adiabatic and isothermal conditions (Harman’s method).

\[
\frac{\delta V_{ad}}{\delta V_{iso}} = \frac{S^2 T}{\rho_s \left( \kappa_s + \kappa_g \frac{t_g}{t_s} \right)} + 1 \tag{2.20}
\]

The empirical FOM for a thin film with a substrate using the modified Harman equation is therefore given by

\[
ZT = \frac{\delta V_{ad}}{\delta V_{iso}} - 1 = \frac{S^2 T}{\rho_s \left( \kappa_s + \kappa_g \frac{t_g}{t_s} \right)} \tag{2.21}
\]
CHAPTER 3
RESULTS AND ANALYSIS

3.1 Predicted Output Profile

If data is collected rapidly, according to Harman’s method, a clear separation between the thermoelectric voltage and resistive voltage should be seen as shown in Figure 3.1. The response of the resistive voltage to the alternating current is fast ($\leq 0.1 \text{ ns}$): therefore, the rise or fall off is not evident for relatively low speeds of data collection. However, the thermoelectric voltage reacts slowly compared to the resistive voltage due to the involvement of heat flowing from one end to the other. Consequently, using an adequate data collection speed should demonstrate the difference between the two voltages for proper analysis.

Figure 3.1: Predicted Output Profile
3.2 Experimental FOM Calculation

Figure 3.2 shows an actual averaged output profile for a square wave input signal of 100 Hz. The figure clearly shows an apparent difference between the thermoelectric voltage and the resistive voltage. By taking the vertical rise of the plot as the isothermal voltage and the peak to peak value as the adiabatic voltage, the experimental FOM can be calculated for each sample with different substrate thickness in all three sample sets, by using the equation

\[
\text{Experimental FOM} = \frac{V_{ad}}{V_{iso}} - 1
\]  

(3.1)

Further, the modified Harman’s method for thin films with substrate gives

\[
\text{Experimental FOM} = \frac{V_{ad}}{V_{iso}} - 1 = ZT_{\text{Expt}} = \frac{S^2T}{\rho_s \left(\kappa_s + \kappa_g t_s / T_s\right)}
\]  

(3.2)

In this study the coefficient of Seebeck \( S \), temperature of the sample \( T \), resistivity of Skutterudite \( \rho_s \), thermal conductivity of Skutterudite \( \kappa_s \), thermal conductivity of glass substrate \( \kappa_g \), and the thickness of the film \( t_s \) are regarded as constants for each sample. The experimental figure of merit \( ZT_{\text{Expt}} \) is the dependent variable and the thickness of the substrate \( t_g \) is the independent variable. This procedure enables us to vary the substrate thickness and observe the variation of the experimental FOM of thin film Skutterudite as it is varied.
3.2.1 Determination of the Absolute Thermoelectric Figure of Merit using a Linear Relation

We define the constants $a$, $b$, and $c$ as follows using the non-variable terms in the section above (3.2).

\[ a = \rho_s \kappa_s, \quad b = \frac{\rho_s \kappa_g}{t_g}, \quad \text{and} \quad c = S^2 T \]  

(3.3)

and thus equation 3.2 becomes

\[ \frac{1}{ZT_{Expt}} = \frac{a}{c} t_g + \frac{a}{b} \]  

(3.4)
which has the form \( y = mx + c \). If we plot \( \frac{1}{ZT_{\text{Expt}}} \) against the substrate thickness \( t_g \), then the reciprocal of \( ZT_{\text{Expt}} \) at zero substrate thickness should be the absolute figure of merit; in other words, the inverse of the intercept directly gives the figure of merit of 40\% La-filled Skutterudite thin film with no substrate.

The following tables contain the empirical FOM and inverse empirical FOM values with the respective substrate thickness for each set of samples. First, the individual measurements for \( V_{ad} \) and \( V_{iso} \) were obtained from thermoelectric and resistive voltage vs time plots as discussed in section 3.2 (Figure 3.2). Substituting these values in equation 3.1 produces the values corresponding to table 3.1. Table 3.2 is obtained by taking the inverse of the experimental FOM values obtained in the previous table (3.1).

As mentioned earlier in section 3.2.1, the experimental FOM value obtained from the modified Harman’s method for laser ablated Skutterudite thin films with substrate is not the limiting FOM of the film itself. The isothermal voltage arising from the Peltier effect and the heat transferred through the material directly affect the measured thermoelectric FOM. When an electric current is applied to the sample, the heat generated flows through the substrate as well as through the Skutterudite sample. Consequently, the apparent FOM value

<table>
<thead>
<tr>
<th>Glass Thickness (mm)</th>
<th>Sample Set 1</th>
<th>Sample Set 2</th>
<th>Sample Set 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \frac{V_{ad}}{V_{iso}} - 1 )</td>
<td>( \frac{V_{ad}}{V_{iso}} - 1 )</td>
<td>( \frac{V_{ad}}{V_{iso}} - 1 )</td>
</tr>
<tr>
<td>0.145</td>
<td>16.67</td>
<td>12.71</td>
<td>14.43</td>
</tr>
<tr>
<td>0.29</td>
<td>13.83</td>
<td>10.69</td>
<td>13.20</td>
</tr>
<tr>
<td>0.435</td>
<td>12.61</td>
<td>9.46</td>
<td>9.54</td>
</tr>
<tr>
<td>0.58</td>
<td>6.11</td>
<td>8.21</td>
<td>8.46</td>
</tr>
</tbody>
</table>
Table 3.2: \( \frac{1}{\text{Expt. FOM}} \) Values with the Respective Substrate Thickness

<table>
<thead>
<tr>
<th>Glass Thickness (mm)</th>
<th>Sample Set 1 ( \frac{1}{ZT_{\text{Expt}}} )</th>
<th>Sample Set 2 ( \frac{1}{ZT_{\text{Expt}}} )</th>
<th>Sample Set 3 ( \frac{1}{ZT_{\text{Expt}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.145</td>
<td>0.06</td>
<td>0.079</td>
<td>0.069</td>
</tr>
<tr>
<td>0.29</td>
<td>0.072</td>
<td>0.094</td>
<td>0.075</td>
</tr>
<tr>
<td>0.435</td>
<td>0.079</td>
<td>0.106</td>
<td>0.105</td>
</tr>
<tr>
<td>0.58</td>
<td>0.164</td>
<td>0.122</td>
<td>0.118</td>
</tr>
</tbody>
</table>

changes with the thickness of the substrate since the heat conduction through the substrate is proportional to its thickness. Figure 3.3 illustrates the dependence of the inverse FOM on the substrate thickness that indicates the result for all 3 sets of samples in the same graph. These 3 curves were extrapolated to find the result at zero thickness, or the limiting FOM value.

Sample set 1:

\[
\frac{1}{\text{Limiting FOM}} = 0.0513 \pm 0.0031^6
\]

Sample set 2:

\[
\frac{1}{\text{Limiting FOM}} = 0.0650 \pm 0.0014^6
\]

Sample set 3:

\[
\frac{1}{\text{Limiting FOM}} = 0.0475 \pm 0.0085^6
\]
3.3 Final Result

The final result obtained from the study as the dimensionless thermoelectric figure of merit for laser ablated 40% La-filled Skutterudite thin films is

Table 3.3: Dimensionless Thermoelectric Figure of Merit

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Dimensionless FOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Set 1</td>
<td>19.56 ± 1.18</td>
</tr>
<tr>
<td>Sample Set 2</td>
<td>15.35 ± 0.33</td>
</tr>
<tr>
<td>Sample Set 3</td>
<td>21.75 ± 3.89</td>
</tr>
<tr>
<td>Overall</td>
<td>18.90 ± 1.43</td>
</tr>
</tbody>
</table>
CHAPTER 4
DISCUSSION AND CONCLUSION

Linear variation of the empirical FOM was observed vs. substrate thickness. The apparent efficiency of the thin films fabricated on tempered glass depends on the thickness of the substrate. As the thickness of the substrate increases the empirical FOM decreases linearly. This is likely due to the increased heat conduction through the substrate. Thicker substrates carrying a higher amount of heat result in a higher figure in the total thermal conductivity of the entire sample. Hence, the assumptions made at constructing the relationship between substrate thickness and experimental FOM for Harman’s method were verified.

4.1 Higher Figure of Merit

Pulsed laser ablated Skutterudite (La$_{0.4}$(Fe$_3$Co)Sb$_{12}$) thin films exhibit higher FOM values compared to the bulk form$^8$ of the same material. The overall value obtained for thermoelectric Figure of Merit in this study approached 18. There can be several possible reasons for higher limiting FOM:

1. Binary Skutterudite (CoSb$_3$) has voids in its crystal structure as shown in Figure 1.4 in Chapter 1. The Skutterudite material used in this study is filled with the Rare Earth element lanthanum up to 40% of its volume. The filler atom is inserted in order to scatter the heat carrying phonons more efficiently compared to unfilled Skutterudite. Moreover, the partial filling of 40% should have a favorable effect on scattering phonons as proven in previous research$^9$ done on thin films. The material investigated has Fe as a substitution in place of Co, creating a more disordered structure as well as producing significant electron-phonon scattering, which would further help reduce the lattice thermal conduction and thus boost the thermoelectric FOM.

2. In Chapter 2 we mentioned that lattice thermal conductivity is the most important
variable in this study. As we predicted a considerable drop in $\kappa_l$ may have occurred. This has the highest probability to take effect compared to other possible effects. Compared to the bulk material, thin films have very low dimensionality. Some past studies\cite{10} have revealed that heat carrying phonons in bulk Skutterudite have a long mean free path. Therefore, with low dimensionality the mean free path of the phonons is reduced due to surface scattering and grain boundary scattering\cite{11}. This would cause the phonons to travel shorter distances than in the bulk, resulting in lower heat transport.

3. Laser ablated films exhibit up to 70% amorphous structure. This could possibly provide a strong contribution to a higher FOM. When producing thin films using the pulsed laser deposition technique, it has been proven that the crystallinity of the target material changes, and the thin film becomes amorphous\cite{12} up to 70%. This may be due to the uneven and disordered deposition of the bombarded Skutterudite atoms on the substrate during laser ablation. This amorphous behavior reduces the lattice portion of the thermal conductivity of the thin film and thus increases the FOM. On the other hand, this amorphous structure may also increase the electrical resistivity of Skutterudite which would decrease the FOM. Due to the dominant effects of amorphous structure on the lattice portion of the conductivity, we expect a higher influence on the lattice thermal conductivity than on the electronic properties.

4. The Seebeck coefficient of thin film Skutterudite can be higher than that of bulk Skutterudite. A small increment in the Seebeck coefficient would directly enhance the thermoelectric FOM due to the square factor contribution. It has been shown that the Seebeck coefficient in thin films is higher than in bulk material due to its size dependence. For thin films, the Seebeck coefficient is found to be temperature dependent, as well as thickness dependent\cite{13}. It decreases with increasing thickness. The thickness dependence of the Seebeck coefficient of simultaneously prepared films
were analyzed using a newer effective mean free path model in previous research, and it has been found that it depends also on material constants such as mean free path, electron concentration, and effective mass of the electrons\textsuperscript{14}. In conclusion, the higher Seebeck coefficient in thin films would produce a larger value of the limiting FOM.

Additionally the variations observed in the empirical thermoelectric FOM in section 3.2 could be due to the non-uniform heat flow through the substrate as shown in Figure 4.1, which would lead to an erroneous estimate of the steady state temperature difference across the sample. There could also be heat losses through the conducting leads, to the surroundings, and to the Teflon support block even though necessary steps were taken to minimize all these adverse effects. The experiment was conducted assuming that the adiabatic conditions prevail throughout the period of data collection; that is, there is no heat exchange between the sample and its surroundings.

![Figure 4.1: Heat Dissipation to Surroundings](image-url)
4.2 Future Goals

At present, most of the modern applications regarding thermoelectric materials are based on thin films rather than on bulk material. The convenience and the effectiveness of these thin films utilized in various practical applications depend on the structure and behavior of the substrate on which the thin film is produced. If it is possible to produce the thin film on a polymer substrate which provides flexibility as an added feature instead of on tempered glass, then the performance and applicability may be increased considerably. Most of the thermoelectric properties vary with absolute temperature. For example, the Seebeck coefficient and thermal conductivity depend strongly on temperature. Hence, it is very important to determine the temperature dependency of the FOM as well. Although in this experiment was conducted at room temperature, the substrate thickness dependence of the FOM could also be observed at higher temperatures up to 200°C. The phonons and electron transport properties vary with temperature fluctuations. Thus may affect the efficiency in different ways. When dealing with higher temperatures, it is crucial to investigate the behavior of the substrate and its characteristics before conducting further thermoelectric experiments.
REFERENCES


