PREPARATION AND CHARACTERIZATION OF

MANGANESE FULLERIDE

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PREPARATION AND CHARACTERIZATION OF MANGANESE FULLERIDE

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ABSTRACT

PREPARATION AND CHARACTERIZATION OF MANGANESE FULLERIDE

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High cooling requirements are of increasing concerns, and means of managing these loads are being sought. Thermoelectric devices offer a unique capability of energy harvesting and providing point cooling utilizing the same device. Commercial thermoelectric materials are based on precious metals or other non-abundant materials. Carbon based fullerene materials have shown great promise for energy conversion applications. With their intrinsically low thermal conductivities, fullerene based materials may offer several advantages for thermoelectric applications over traditional inorganic based thermoelectric materials. Fulleride materials have already shown electrical properties spanning from the insulating to superconductive regimes.

This work focused on preparing and characterizing manganese fulleride(s) by wet chemical synthesis and physical vapor deposition methods, both building on recent analogous zinc fulleride work. Characterization of the wet synthetic powders revealed fullerols were produced instead of fullerides. Consequently, the resulting material(s) was found to be unsuitable for thermoelectric applications. Deposition samples yielded more favorable results for both characterization and material properties. The resulting room
temperature $zT$ was determined to be $6.0 \cdot 10^{-6}$. In all cases, electrical conductivities and thermopowers require improvement if manganese fulleride(s) are to be considered as viable thermoelectric material.
I would like to dedicate this work to my family, my friends, and my mentors without whom this work would not be possible.
ACKNOWLEDGEMENTS

I would not have been able to complete this work without the help and guidance of many individuals. I would like to this time to thank those who helped me along the way beginning with those who I worked with daily, mainly those in the former Thermal Sciences and Materials Branch in the Materials and Manufacturing Directorate of the Air Force Research Laboratories at Wright-Patterson Air Force Base. I would like to thank, but not limited to: “Team Fulleride,” consisting of Dr. Douglas Dudis, Dr. David Turner, and Michael Check, continually assisted me with technical assistance and guiding advice. Additionally, I would like to thank Dr. Doug Dudis for serving as my research advisor and Dr. David Turner for serving as my mentor during this work. I would like to thank Dr. Michael Jesperson for his assistance with XPS and its subsequent analysis and Adam Brant for performing EPR of my powders. Also, I would like to thank Marlene Houtz for performing MDSC of my samples and Dr. Jamie Gengler for performing and modeling TDTR results. Next, I would like to thank Aaron Sprague for assisting with laser flash analysis and Matt Dalton for assisting my with IR spectroscopy. Lastly, I would like to Art Safriet and Travis Shelton for their help with tooling and building the bulk thermopower device. A special consideration would like to be given to Nicholas Glavin, John Bultman, and Dr. Steve Patton for their assistance.

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inspiration to pursue a graduate degree and for providing academic advice throughout my higher education process. I would also like to thank Dr. Robert Wilkens and Dr. Charles Browning for serving on my members.

Two additional acknowledgements would like to be given for continually motivation during this work. First I would like to thank Pandora (and eventually Pandora One) for acoustical motivation no matter the time of day or night. Without this stimulation many hours would have been lost to lack of focus or sleep. Second, I would like to thank J. K. Rowling’s Harry Potter. Harry Potter changed life and I feel that I am better for it. Though I was not able to cast a successful wingardium leviosa or expecto patronum, I did succeed at boiling cauldrons in the lab thanks to Harry.

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<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>TE</td>
<td>Thermoelectric</td>
</tr>
<tr>
<td>S</td>
<td>Thermopower, or Seebeck coefficient [V/K]</td>
</tr>
<tr>
<td>V</td>
<td>Voltage difference [V]</td>
</tr>
<tr>
<td>ΔT</td>
<td>Temperature difference [K]</td>
</tr>
<tr>
<td>Π</td>
<td>Peltier coefficient [V or J/C]</td>
</tr>
<tr>
<td>I</td>
<td>Current [A]</td>
</tr>
<tr>
<td>η</td>
<td>Carnot efficiency</td>
</tr>
<tr>
<td>W</td>
<td>Work [W]</td>
</tr>
<tr>
<td>Q</td>
<td>Heat flow [W]</td>
</tr>
<tr>
<td>R</td>
<td>Resistance [Ω]</td>
</tr>
<tr>
<td>K</td>
<td>Thermal conductance [W/K]</td>
</tr>
<tr>
<td>T_H</td>
<td>Warm side of TE device [K]</td>
</tr>
<tr>
<td>T_C</td>
<td>Cool side of TE device [K]</td>
</tr>
<tr>
<td>T̅</td>
<td>Average temperature of TE device [K]</td>
</tr>
<tr>
<td>σ</td>
<td>Electrical conductivity [1/(Ω · m)]</td>
</tr>
<tr>
<td>κ</td>
<td>Thermal conductivity [W/(m · K)]</td>
</tr>
<tr>
<td>ZT</td>
<td>Dimensionless TE figure of merit for a device</td>
</tr>
<tr>
<td>zT</td>
<td>Dimensionless TE figure of merit for a material</td>
</tr>
<tr>
<td>κ_e</td>
<td>Electronic contribution to thermal conductivity [W/(m · K)]</td>
</tr>
<tr>
<td>κ_l</td>
<td>Lattice contribution to thermal conductivity [W/(m · K)]</td>
</tr>
<tr>
<td>PGEC</td>
<td>Phonon Glass, Electron Crystal</td>
</tr>
<tr>
<td>κ_min</td>
<td>Minimum thermal conductivity if all phonons have mean free path equal to one wavelength [W/(m · K)]</td>
</tr>
<tr>
<td>U</td>
<td>Weighted mobility [cm²/(V · s)]</td>
</tr>
<tr>
<td>μ</td>
<td>Carrier mobility [cm²/(V · s)]</td>
</tr>
<tr>
<td>m*</td>
<td>Density of states effective mass [kg]</td>
</tr>
<tr>
<td>m₀</td>
<td>Free electron mass [kg]</td>
</tr>
<tr>
<td>E_g</td>
<td>Band gap [eV]</td>
</tr>
<tr>
<td>k_B</td>
<td>Boltzmann constant [8.617 · 10⁻⁵ eV/K]</td>
</tr>
<tr>
<td>T</td>
<td>Temperature [K]</td>
</tr>
<tr>
<td>n</td>
<td>Electron concentration [1/m³]</td>
</tr>
<tr>
<td>e</td>
<td>Electron charge [C]</td>
</tr>
<tr>
<td>RTG</td>
<td>Radioisotope thermoelectric generator</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>ρ</td>
<td>Density [g/m³]</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight [g/mol]</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive spectroscopy</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MDSC</td>
<td>Modulated differential scanning calorimetry</td>
</tr>
<tr>
<td>PSM</td>
<td>Potential-Seebeck microprobe</td>
</tr>
<tr>
<td>TDTR</td>
<td>Time-domain thermal reflectance</td>
</tr>
<tr>
<td>ΔE</td>
<td>Energy [J]</td>
</tr>
<tr>
<td>h</td>
<td>Plank’s constant ([6.626 \cdot 10^{-34} \text{ (J \cdot s)}])</td>
</tr>
<tr>
<td>v</td>
<td>Microwave frequency [GHz]</td>
</tr>
<tr>
<td>g</td>
<td>Electron g-factor [unitless]</td>
</tr>
<tr>
<td>(\mu_B)</td>
<td>Bohr magneton ([9.274 \cdot 10^{-24} \text{ J/T}])</td>
</tr>
<tr>
<td>(B_0)</td>
<td>Magnetic field strength [G]</td>
</tr>
<tr>
<td>(C_p)</td>
<td>Heat capacity ([\text{J/(kg \cdot K)}])</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>Thermal diffusivity ([\text{m}^2/\text{s}])</td>
</tr>
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</table>
CHAPTER I
INTRODUCTION

1.1. Energy Management Motivation

The Air Force’s motivation for energy management encompasses ever increasing thermal loads associated with Air Force platforms. The management of these loads has become one of the limiting factors for modern and future systems as shown in Figure 1. Electronic components continue to be one of the primary heat loads requiring cooling. Traditional means, forced convection and liquid cooling, are inadequate to address the need for thermal management, and new strategies and technologies are being sought to fill the void.1

![Figure 1: Thermal loads and technologies employed for Air Force platforms](image)
The semiconductor industry is increasingly concerned with energy management. Gordon Moore, the co-founder of Intel, predicted the number of silicon transistors in processors would double every 24 months, the so-called “Moore’s Law.”\textsuperscript{2} As can be seen in Figure 2, this prediction has a high fidelity with processor development.

**Figure 2: Transistor count in microprocessors since 1971\textsuperscript{3}**

The thermal implications of Moore’s Law are profound. Assuming the heat load associated with transistors is generated solely by Joule heating, CPU thermal loads can be readily estimated (Figure 3). Extrapolation from the data in Figure 3 indicates that by ~2015 the heat flux (power density) for a single CPU microprocessor would have exceeded the heat flux for the surface of the sun (~6000 W/cm\textsuperscript{2}).\textsuperscript{4} This was a major motivation for the advent of multicore processors. The transformation in the microprocessor industry provides insight into the underlying origins of a number of Air Force thermal management problems where space and weight are additional concerns.
Avionics aren’t the only energy and thermal management limitation the Air Force is facing. Forward operating bases currently attribute ~60% of their energy consumption to heating and cooling, a form of thermal management. Since one of the largest sources of injuries and fatalities can be attributed to transporting fuel to forward bases, reduced energy consumption and waste energy harvesting are being considered.

1.2. Air Force Energy Approaches

The Air Force has employed, for avionics platforms, forced convection while in flight to cool key components on aircraft. Thermal loads have also been mitigated by rejecting heat into jet fuel. However, current and future systems need new approaches for thermal management. Phase change materials, including waxes and liquids/solids to vapor/fluids, are proposed solutions for thermal energy management. Phase change materials allow for reusable or expendable energy storage media. These materials
possess the ability to act in tandem with existing technologies to absorb peak loads.

Thermoelectric (TE) technologies are also being pursued. TE devices have been proposed to utilize thermal waste from engine exhaust and provide point cooling to circuitry.\textsuperscript{6} TE technologies are also being examined for forward bases in cooling of tents and cots as a means to reduce overall forward operating base energy consumption.
CHAPTER II

RESEARCH OBJECTIVES

Ongoing work within AFRL is focused on a subset of promising TE materials based on metal fullerides. The fulleride structure of current interest is a charged Buckminster fullerene cage, \( \text{C}_{60}^n \), with \( n = 1 \) to 6.\(^7\) The objective of this thesis is to expand upon previous work involving zinc fullerides by incorporating manganese instead of zinc. Manganese is of interest for several reasons. First, manganese, like zinc, is low cost, abundant, and non-toxic unlike currently utilized Bi\(_2\)Te\(_3\). Second, manganese does not have a filled d\(^{10}\) manifold. Subsequently, manganese possesses multiple oxidation states, unlike zinc, and can be paramagnetic as can fullerides. With the inclusion of paramagnetic ions, there is interest in examining spin-spin interactions for possible TE enhancement.\(^8\) Lastly, manganese’s oxidation potential is in the correct range for redox chemistry with C\(_{60}\). Specific goals of this thesis include:

1. Preparation of manganese fulleride(s) by wet synthetic approaches
2. Preparation of manganese fulleride(s) by physical vapor deposition approach
3. Confirmation and characterization of manganese fulleride(s)
4. Investigation whether manganese fulleride(s) will pose as an acceptable TE material

Wet synthetic chemistry and physical vapor deposition techniques were employed to prepare the manganese fulleride materials which were characterized using scanning
electron microscopy, energy-dispersive spectroscopy, Raman spectroscopy, electron paramagnetic resonance, X-ray photoelectron spectroscopy, infrared spectroscopy, modulated differential scanning calorimetry, laser flash analysis, four point probe resistance measurements, thermopower measured using a bulk Seebeck device or potential-Seebeck microprobe, and time-domain thermal reflectance measurements.
CHAPTER III

LITERATURE REVIEW

3.1. Introduction to Thermoelectrics

TE modules are solid state energy conversion devices fabricated from multiple p-n junctions connected in series electrically but connected in parallel thermally. Present TE technologies are ~10-12% thermodynamically efficient using bulk materials. Most commonly, TE’s are used in either the Seebeck or Peltier mode which is described below.

3.1.1. Seebeck Effect and Energy Harvesting

In 1821 Thomas Seebeck, a German physicist, began experimenting with temperature gradients and magnetism. He demonstrated that by connecting two dissimilar metals in a closed loop and applying a thermal load to one of the junctions, a compass needle could be deflected. Much later it was realized the deflection of the needle was caused by induced magnetism of a thermally induced electrical current, rather than a magnetic-thermal effect as originally postulated by Seebeck. A simple Seebeck circuit is illustrated in Figure 4.
Figure 4’s circuit contains two junctions of the dissimilar materials. By thermally disturbing one junction, a voltage difference is established across the materials by a redistribution of the charge carriers. Seebeck devised a mathematical expression relating the voltage produced by a temperature gradient to a property named thermopower, or Seebeck coefficient. This expression for thermopower is shown in Equation 1.

\[
S = \frac{V}{\Delta T}
\]  

(1)

Physically the voltage results from the charge carriers, electron/holes, becoming excited from the thermal input and redistributing to establish a new equilibrium. The newly formed equilibrium results, for an open circuit, with a greater distribution of charge carriers on the cooler end of the material. By closing the circuit, as shown in Figure 5, power generation can be obtained.\textsuperscript{14} Traditional TE material p-n junctions generate on the order of mV; therefore, multiple p-n junctions connected in series are required to produce practical voltages.\textsuperscript{15} Notable examples employing TE energy harvesting devices are Voyager 1, which is operating in deep space 35 years after its launch, up to NASA’s latest Martian rover, Curiosity.\textsuperscript{13}
3.1.2. Peltier Effect and Refrigeration

In 1834 Jean Charles Peltier, a French physicist, discovered the relationship between heating and cooling when an electric current was passed through a junction of dissimilar metals. This effect would be subsequently named the Peltier effect. The mathematical expression Peltier derived is shown in Equation 2. It relates the heat flow through the junction to the magnitude of current and the Peltier coefficient. Lord Kevin would 20 years later relate the Peltier coefficient to thermopower.\(^\text{10}\)

\[
\dot{Q} = \Pi \cdot I = (S \cdot T) \cdot I
\]  

(2)

The direction of the current from Equation 2 determines the thermal response at the p-n junction. If the electron current flows from the n-type to the p-type material, the junction is cooled. Heating will occur at the junction if the current direction is reversed.\(^\text{14}\) This concept is illustrated in Figure 6. Temperature differences between the sides of the device can be \(\sim 50^\circ\text{C}\) with this device architecture and current technology.\(^\text{10,16}\) Devices providing active cooling and/or heating have been utilized in niche markets such as
temperature control on sensitive diodes in optoelectronics and for passenger seat heating and cooling in the automobile industry.\textsuperscript{17}

![Diagram of active cooling device](image)

**Figure 6: Device architecture for active cooling**

### 3.1.3. Thermoelectric Figure of Merit

TE devices are heat engines and thermodynamically bound by the Carnot limits. Deriving the Carnot efficiency results in a dimensionless figure of merit, ZT and which has been the focus of optimization for the last 30 years. Starting with the definition of Carnot efficiency, $W/Q$, the work component can be described by two terms: the Seebeck term and the Joule heating. The heat flow through the engine can be attributed to three sources: thermal conductance through the material, Peltier effects, and heat loss due to Joule heating effects.\textsuperscript{18}

\[
\eta = \frac{W}{Q} = \frac{I_S \Delta T - I^2 R}{K \Delta T + I_S T - I^2 R} \tag{3}
\]
To maximize $\eta$, the first derivative of Equation 3 with respect to current is set to zero. Substituting the $I_{\text{max}}$ back into Equation 3 and rearranging, Equation 4 can be derived.\textsuperscript{15,19}

$$\eta = \frac{T_H - T_C}{T_H} \cdot \sqrt{\frac{1 + \frac{S^2 \sigma \cdot T}{R K} - 1}{1 + \frac{S^2 \sigma \cdot T}{R K} + \frac{T_C}{T_H}}}$$

(4)

There is a dimensionless term appearing twice in $\eta$. By making the following substitutions, $K$ to $(\kappa \cdot m)$ and $1/(R \cdot m)$ to $\sigma$, the TE figure of merit, $ZT$, can be written as shown in Equation 5.

$$\frac{S^2 \sigma}{R K} = \frac{S^2 \sigma}{\kappa} \frac{T}{\text{¯}} = ZT$$

(5)

It is important to note that $ZT$ was derived at the device level. The $ZT$ for a device will be smaller than the $zT$ of its components due to electrical resistances losses and thermal shorts. A material’s $ZT$ can be expressed by Equation 6. From here on $zT$ discussion will be restricted to the material level.

$$zT = \frac{S^2 \sigma}{(\kappa_e + \kappa_l)} \frac{T}{\text{¯}}$$

(6)

In Equation 6 the thermal conductivity has been separated into its two major components: the electronic contribution and the lattice (vibrational) contribution. A third component, bipolar thermal conductivity, is typically neglected if the band gap is greater than $10k_B T$, which is the typical case for standard TE materials.\textsuperscript{20}

**3.2. Thermoelectric Materials Review**

In the 1950s Ioffe proposed that binary and ternary semiconductors formed from heavy elements would be the best TE materials.\textsuperscript{21} Such materials have been a focus of TE research as evident in the overview of state-of-the-art TE materials shown in Figure 7.
Commercially available TE modules are fabricated using p- and n-type Bi$_2$Te$_3$. High temperature SiGe modules used in deep space probes are not commercially available. Since the 1993 publication of Hicks and Dresselhaus, a renaissance in the search for TE materials has occurred. The current focus on global energy needs adds further emphasis.

3.2.1. Phonon Glass, Electron Crystal

In 1995 Slack proposed that optimal TE materials should resemble a phonon glass and an electron single crystal. A phonon glass, electron crystal (PGEC) material would exhibit ideal qualities with respect to thermal conductivity, electrical conductivity, and thermopower.

Glasses are characterized by low thermal conductivities. Typical values are on the order of 1 W/(m · K) and are attributed to the lack of long range atomic order. With this type of atomic structure, phonons, which are responsible for thermal transport, are readily scattered. Scattering phonons effectively results in phonon mean free paths on the order of atomic dimensions and consequently low thermal conductivity values.
The other attributes for Slack’s ideal PGEC is a material that is electrically crystalline. This would require electron mean free paths to be as long as possible. With long mean free paths, electrons would travel with little resistance; thereby, the electrical conductivity would remain high.

Through examination of existing TE materials, Slack generated three criteria that need to be met in order to obtain a PGEC which could achieve a zT value of 4. Upon assuming that carrier mobility, lattice thermal conductivity, and effective mass are independent of carrier concentration and that thermal conductivity and effective mass are also independent of temperature, Slack’s criteria include:

1. thermal conductivity: \( \kappa_L = \kappa_{\text{min}} = \text{constant} ( = 0.25 \text{ W/(m \cdot K)} \) for PbTe

2. band gap: \( E_g \geq 10k_B T \) ( = 0.25 eV at 300 K for materials)

3. weighted mobility: \( f(\text{carrier mobility, effective mass}) = U = \mu(m^*/m_0)^{1.5} \)

Slack’s first criterion addresses the issue of minimizing thermal conductivity, or limiting thermal shorts. This criterion is based on the mean free path of phonons though a material being reduced to one wavelength. Slack later addresses means of reducing the thermal conductivity by reducing phonon mean free path. These strategies include: mixed-crystal samples, possessing atoms/groups in a crystal with orientations not completely defined, rattling atoms/groups with no long-range correlations in a crystal, and the mass of rattling atoms/groups being \( \geq 3\% \) of the total crystal mass. The assumption of a constant thermal conductivity value will hold true for heavier elements or compounds at temperatures greater than \( \sim 100 \text{ K} \). Most heavier element semiconductors have minimum thermal conductivity values on the order of 0.1 to 0.5 W/(m \cdot K).
Slack’s second criterion focuses on the efficiency of converting thermal energy to electrical energy. Slack states that it is necessary for TE materials to exhibit thermopowers greater than 100 µV/K. Semiconductors best fit this requirement. Consequently, prior work by Mahan has shown an optimum band gap for TE semiconductors should be 10k_BT.\textsuperscript{37,38} Deviation from this range results in negative consequences summarized below:

- Larger band gaps: mobilities tend to decrease or thermal conductivities tend to increase, or both
- Smaller band gaps: thermopowers tend to decrease and the bipolar thermal conductivity increases

Slack’s third criterion addresses charge transport in the TE material. For optimum performance the electron crystal material should exhibit high electrical conductivities, and subsequently high carrier mobility through their relationship shown in Equation 7.\textsuperscript{39}

\[ \sigma = n \cdot e \cdot \mu \]  

(7)

The second component to weighted mobility is the density of states effective mass divided by electron free mass. Slack further assumed a single valence and conduction band. Incorporating empirical observations, low values for weighted mobility were determined to be poor TE materials whereas high values indicated a probability of a good TE. A conclusion that was drawn related the electronegativity differences to the weighted mobility. For weighted mobility values to be in the desired order of magnitude, electronegativity differences between the elements in a binary or ternary compound had to remain small.
3.2.1.1. Skutterudites

After the PGEC concept had been proposed, research began to find materials to test Slack’s hypotheses. One of the first classes of materials investigated was skutterudites, which discovered in 1977 by Jeitschko and Braun.\textsuperscript{40,41} Skutterudites were of TE interest due to their complex crystal structure as shown in Figure 8. The general formula for skutterudites is $LT_4X_{12}$ where $L$ is typically a first row lanthanide element (La, Ce, Pr, Nd, or Eu), $T$ is a Group 8 transition metal (Fe, Ru, or Os), and $X$ is a Group 15 element (P, As, or Sb). Skutterudites are believed to satisfy PGEC criteria in three ways.

![Filled skutterudite crystal structure for LaFe$_4$Sb$_{12}$ where grey spheres are La$^{3+}$, black spheres are Fe$^{2+}$, and planar white spheres are Sb$^{4-}$.](image)

Figure 8: Filled skutterudite crystal structure for LaFe$_4$Sb$_{12}$ where grey spheres are La$^{3+}$, black spheres are Fe$^{2+}$, and planar white spheres are Sb$^{4-}$.\textsuperscript{42}

The Group 15 elements, referred to as filler atoms, are ionically bound inside the framework formed by $T$ elements. Consequently, the filler atoms do not directly affect the electrical transport appreciably. However, the filler atoms do contribute significantly
to the phonon scattering abilities, especially when the filler atoms are heavy such as antimony.

The choice of the transition metal used for the lattice framework can greatly influence the electrical conductivity. For instance, substitution of iron by cobalt in CeFe$_{4-x}$Co$_x$Sb$_{12}$ with $x=1$ increases the $zT$ significantly and is projected to achieve $zT=1.4$, after optimization.\textsuperscript{40} This is believed to be a result of an extra electron contributed to the conduction band and modifying the band gap slightly. It was reported that increasing the cobalt fraction further distorted the lattice and resulted in blocking the lanthanide, Ce, from its interstitial sites.

Another major focus of skutterudite research has been the light rare earth elements in the crystal structure. The majority of these studies have examined the atomic replacement of one element for another.\textsuperscript{43} However, promising developments were found with the partial filling of the skutterudite structure with the lanthanides.\textsuperscript{44,45} Partial filling of the interstitial sites was reported to lower the lattice thermal conductivity of the skutterudite. Conclusions were drawn that partial filling could allow for increased phonon scattering from the defect sites. It was also observed that for partially filled structures, the carrier motilities and thermopowers were greatly affected. For example in La$_x$Co$_4$Sn$_y$As$_{12-y}$ the carrier type changed from p-type to n-type and back as $x$ increased. The resulting room temperature thermopowers varied from 190 $\mu$V/K (at $x = 0$) to -165 $\mu$V/K (at $x = 0.05$) and back to positive values ($x > 0.31$).\textsuperscript{44}

### 3.2.1.2. Zintl Phases

Zintl phases are also of interest as potential PGEC abilities. Zintl phases, which were first described in the 1930s, combine complex structuring with a small
Electrical transport is propagated along covalent bonds of carrier rich elements while cations are bound ionically in the lattice and provide scattering of the phonons which lowers the lattice thermal conductivity. Two types of zintl phases have shown promise for TE properties. The first representative structure is shown in Figure 9. The general formula for this zintl phase is $A_{14}MX_{11}$ where $A$ is a heavy or alkaline earth metal, $M$ is a transition metal, and $X$ is, once again, a Group 15 element (P, As, Sb, or Bi).

![Figure 9: Representative crystal structure of $A_{14}MX_{11}$. Specifically crystal structure of $Yb_{14}MnSb_{11}$ where black spheres are $Yb^{2+}$, white spheres are $Sb^{3-}$, linearly bound white spheres are $Sb_{3}^{7-}$, and grey tetrahedrals are $[MnSb_{4}]^{10-}$](image)

Examination of Figure 9 reveals $Yb_{14}MnSb_{11}$ possesses a variety of distinct motifs within the unit cell. The lattice thermal conductivity for the material is subsequently low, 0.4 W/(m · K), and provides the phonon glass capacity desired in Slack’s ideal material. The thermopower is positive (p-type), a rarity among high performance TE materials, and report to continue increasing up to 1300 K. The electrical
conductivity decreases with increase temperature, as expected, to a minimum at value at 1200 K. These properties combine to give Yb$_{14}$MnSb$_{11}$ a zT value of 1 at 900 °C, as seen in Figure 7 (right). The zT value was twice that of SiGe which is used in radioisotope thermoelectric generators (RTGs) from NASA to power spacecraft. This generated substantial interest as a possible replacement to SiGe alloys in TE devices.

Manipulation of the stoichiometry has been shown to improve the electric and thermal contributions. Specifically incorporating atomic substitutions into the M and/or X sites can tune the carrier concentration or lower the lattice thermal conductivity by increased phonon scattering. In practice these zintl phases have proved to be moisture and air sensitive. Consequently, the antimony variations of this zintls have garnered the most focus because of their air stability.

A different zintl phase with a 2 dimensional character also shows TE promise. The Ca$_x$Yb$_{1-x}$Zn$_2$Sb$_2$ crystal structure is representative of this class of zintl complexes, see Figure 10. The Zn-Sb planes allow for high electrical transport with their covalent bonding. The electronegativities of Zn and Sb are similar; thereby, the plane expresses a low polarity and is able to allow for high hole mobility. The inclusion of Ca cations provides the material a band gap of 0.25 eV, while the Yb cations make the structure slightly electron deficient (much like the skutterudites) and cause the material to become strongly p-type with metal-like transport properties. There is also a notable reduction in the lattice thermal conductivity from the alloying effect of two cations on the phonons resulting in a zT of over 1 around 700 K; but, the zintl still has high lattice thermal conductivity, 1.5 W/(m · K). The drawback to the layered zintls are no long range disordering, so long-wavelength phonons are not scattered. It has been suggested that the
zintl phase could be nanostructured or used in hierarchical structures to reduce the thermal contribution and ultimately improve $zT$.\textsuperscript{22}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{Crystal structure of $\text{Ca}_x\text{Yb}_{1-x}\text{Zn}_2\text{Sb}_2$ where white spheres are a disordered sheet of cations ($\text{Ca}^{2+}$ or $\text{Yb}^{2+}$) and grey and black spheres are $\text{Sb}$ and $\text{Zn}$, respectively, in their covalently bound $[\text{Zn}_2\text{Sb}_2]^2-$ plane.\textsuperscript{42}}
\end{figure}

\textbf{3.3. Introduction to Fullerides}

The quest for new TE materials is motivated in part by the need for higher efficiencies. To be economically viable, it is preferable to not rely on non-abundant elements. With 99\% of the earth’s crust containing the rock-forming elements, the economic feasibility of large scale TE manufacture based on precious metals, such as tellurium, is uncertain.\textsuperscript{48} According to Yadav, while these materials have been shown to exhibit high $zT$ values, materials based on metal oxides or other rock-forming elements may prove to be more viable for manufacturing.\textsuperscript{49}
Carbon is several orders of magnitude more abundant than precious metals or rare earth metals, and the electrical and thermal properties of carbon structures are not inhibitive to TE applications. As shown in Table 1, doped C\textsubscript{60}’s electrical properties show significant improvement over pristine C\textsubscript{60}. The thermal conductivity of the C\textsubscript{60} during the doping typically remains relatively unchanged, paralleling the PGEC model.\textsuperscript{51}
Table 1: Order of magnitude of the room temperature electrical conductivity of various forms of carbon

<table>
<thead>
<tr>
<th>Order of Magnitude of Electrical Conductivity at 300 K [1/(Ω · m)]</th>
<th>Material</th>
<th>Type of Conduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁸ – 10⁷</td>
<td>Graphite intercalation compounds (in plane)</td>
<td>Metallic</td>
</tr>
<tr>
<td>10⁶</td>
<td>Pristine highly ordered pyrolytic graphite (in plane)</td>
<td>Semimetallic</td>
</tr>
<tr>
<td>10⁵</td>
<td>Some Nanotubes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Doped C₆₀</td>
<td>Semimetallic</td>
</tr>
<tr>
<td>10³ – 10²</td>
<td>Acceptor graphite intercalation compounds (out of plane)</td>
<td>Not yet defined</td>
</tr>
<tr>
<td></td>
<td>Pristine highly ordered pyrolytic graphite (out of plane)</td>
<td></td>
</tr>
<tr>
<td>&lt; 10⁻¹⁸</td>
<td>Doped diamond</td>
<td>Semiconducting</td>
</tr>
<tr>
<td></td>
<td>Pure diamond</td>
<td>No conduction</td>
</tr>
<tr>
<td></td>
<td>Pristine C₆₀</td>
<td>No conduction</td>
</tr>
<tr>
<td></td>
<td>Some nanotubes</td>
<td>No conduction</td>
</tr>
</tbody>
</table>

Fullerenes are caged structures formed from sp² hybridized carbons or similar atoms. Fullerene π orbitals are extensively delocalized over the surface of the molecular cage. Of the fullerenes C₆₀ (Figure 12) is the most readily available, followed by C₇₀ and then higher order fullerenes, such as C₇₆, C₇₈,… with the largest to date stable fullerene being C₈₄. The C₆₀ structure contains 20 hexagonal rings and 12 pentagonal rings. The crystal structure of C₆₀ has been determined to be face center cubic at room temperature and simple cubic below 256 K. This packing configuration, with a molecule so large, allows for large interstitial sites within the lattice.
Fullerenes and fullerides have been the focus of many investigations for energy applications and to a lesser extent thermal applications. The thermal conductivities for fullerides are typically very low; for example the thermal conductivity of PC₆₀ is on the order of 0.1 W/(m · K). The low thermal conductivity has been largely attributed to C₆₀’s low Debye temperature. Under Debye assumptions the vibrations of the lattice are considered to be phonons and the carriers of thermal energy. C₆₀ has an available 46 symmetry independent vibrational modes. However, these vibrations are between C-C bonds, localized within the molecular cage, whereas the phonon vibrations are between the C₆₀ molecules. The majority of the thermal energy in a fulleride is stored within the vibrations of the molecular framework and only couple weakly to the lattice phonons. Consequently, fullerenes and fullerides have ultra-low thermal conductivities.

### 3.3.1. Current Fullerides

Fullerides are charged compounds formed from fullerenes and other elements. The C₆₀ cage can readily accommodate up to six electrons, sometimes as many as 12, allowing for a plethora of fulleride stoichiometries. Fullerides have been most commonly formed by doping with alkali and alkaline earth metals. However, some fulleride complexes have been formed with transition and rare earth metals.
3.3.1.1. Alkali Fullerides

Doping $C_{60}$ with alkali metals has arguably sparked the most interest in fulleride materials, the most notable being potassium doped $C_{60}$.\textsuperscript{61-63} $K_3C_{60}$ was the first fulleride found to be superconducting. A doping study conducted by Holczer, et al. revealed that only the $x = 3$ stoichiometry of $K_xC_{60}$ becomes superconducting.\textsuperscript{61} The onset of the superconducting regime was determined to be at 20 K, which is one highest molecular based temperatures for superconductivity. Typical fulleride superconductivity temperatures are between 1 and 20 K, but using a larger alkali element, rubidium, further raised the superconducting regime to 28 K with $Rb_3C_{60}$.\textsuperscript{61} Alkali dope fullerides are not chemically stable under atmospheric conditions.

3.3.2. Alkaline Fullerdies

Fullerides can also be formed with alkaline earth metals. Alkaline earth fullerides tend to adopt a body centered cubic lattice whereas the alkali fullerides remain in the face centered cubic or simple cubic lattice. The consequence of the body centered cubic lattice is an increase in the number of interstitial sites from 3 to 6. An example of the fully filled interstitial sites is $Ba_6C_{60}$ which was examined by Shi, et al. $Ba_6C_{60}$ was reported to have a low thermopowers, from -15 to -35 $\mu$V/K at 300 K to 850 K respectively.\textsuperscript{60} At the same time, the electrical conductivity was moderate, 250 to 150 $1/(\Omega \cdot m)$ over the same temperature range. The low thermopowers were attributed to the metallic nature exhibited by the fulleride and the major inhibiting factor to TE application according to Shi, et al.
3.3.2.1. Transition Metal Fullerides

Transition metal fullerides have yet to spark strong interest as seen in alkali metals. Transition metal fullerides reported to date include: \( \text{Ni}_x\text{C}_{60}, \text{Co}_x\text{C}_{60}, \text{Nb}_x\text{C}_{60}, \text{Pd}_x\text{C}_{60}, \text{Pt}_x\text{C}_{60}, \text{Fe}_x\text{C}_{60}, \text{Zn}_x\text{C}_{60}, \text{and Mn}_x\text{C}_{60}. \)\(^{57,59,64-68}\) Not all of the transition metal fullerides have been examined for TE properties; however, those that were typically had thermopowers too low for effective TE application (below \( |15| \mu\text{V/K} \)), and vary from element to element along with their electronic structure, p-type or n-type. Check et.al, determined that thermal conductivity of \( \text{Zn}_x\text{C}_{60} \) remained ultra-low and the electrical conductivity was 430 \( 1/(\Omega \cdot \text{m}) \).\(^{65}\)

3.3.2.2. Group 15 Fullerides

Group 15 elements can dope fullerenes, reminiscent of skutterudites with antimony. \( \text{PC}_{60} \) exhibits a very high thermopower (1740 \( \mu\text{V/K} \) at 300 K) while retaining very low thermal conductivity, see Figure 13; however, there is concern about the lattice stability. The thermopower was reported to decrease over time at moderately high temperatures due to phosphorous being pushed out of the lattice. Increasing the doping level to \( \text{P}_4\text{C}_{60} \) resulted in a reduced thermopower (3 \( \mu\text{V/K} \) at 300 K), thereby suggesting only a slight doping of phosphorous and 300 K applications. Doping with a heavier Group 15 element, bismuth, results in \( \text{BiC}_{60} \) which does not show a large thermopower. The band structure of \( \text{BiC}_{60} \) shows a lower carrier activation energy. Consequently, the thermopower is only 22 \( \mu\text{V/K} \) at 300 K compared to \( \text{PC}_{60} \)'s 1740 \( \mu\text{V/K} \). In both cases however, the materials are too resistive for TE applications.\(^{59}\)
3.3.3. Summary

C$_{60}$ based materials continue to be of interest to TE researchers. Fullerides have the potential to fulfill the PGEC model proposed by Slack. The thermal conductivities of C$_{60}$ base materials approach the proposed $\kappa_{\text{min}}$. This is a result of weak coupling of C-C cage vibrations with lattice phonons. The key to fulleride thermopowers and electrical properties are the doping elements and levels chosen. Proper selection can enable fullerides to exhibit very high thermopowers (PC$_{60}$) or high electrical conductivities (to the point of superconducting in alkali fullerides).
CHAPTER IV
CHARACTERIZATION

4.1. Scanning Electron Microscopy and Energy-Dispersion Spectroscopy

Scanning electron microscopy (SEM) was performed using a Hitachi Tabletop TM3000 and a FEI Quanta 600F SEM. The Quanta SEM produced higher quality images and was used where in-depth examination was required. Otherwise due to availability and fine resolution not being required (images below 5000x or 24 µm x 32 µm) the Hitachi SEM was used. In either case, wet chemical powders were adhered to carbon dots and excess material removed by compressed gas prior to examination. Physical vapor depositions (PVD) samples were examined using a clipping substrate holder.

Energy-dispersive spectroscopy (EDS) was performed using a Bruker Quantax 70 EDS detector attached to the Hitachi TM3000. The detector operated at 15 kV at distance of ~9.2 mm from the sample. EDS was carried out 500x magnification for 5 minutes. Elemental percentages were averaged from five locations across the acquired image and a minimum of two image locations were examined.

4.2. Raman Spectroscopy

Raman spectra for films and powders were recorded using a Renishaw inVia Raman Microscope with 514 nm excitation wavelength. A range of 100-2000 cm$^{-1}$ was
examined with cosmic ray removal enabled. The laser power and length of scan were adjusted to allow for the greatest signal to noise ratio. Typical laser powers settings were 1% to 10% of total laser power and typical scan times were 10 s to 40 s. Scans were taken on silicon wafers which only exhibit a peak at 520 cm⁻¹; thereby ensuring all peaks observed were associated with powders or films. Multiple scans were taken and the results were added internally to further improve the signal to noise ratio. Scan results were exported to Microsoft Excel for graphing and background removal. Peak analysis and deconvolution were carried out using OriginPro 8.5 utilizing the raw data and OriginPro’s background removal routines. Subpeaks were characterized using Lorentzian functions. The number of subpeaks allowed was constrained to conform to literature peak degeneracies for similar materials.

4.3. Electron Paramagnetic Resonance

Electron paramagnetic resonance (EPR) spectra were reported on powders using a Bruker EMX system. The microwave operating frequency was maintained ~9.4 GHz. The system was liquid helium cooled with an Oxford Helium Gas Flow System. The practical lowest operating temperature for the system was 4 K. A nitrogen gas stream was blown into the sample cavity to manipulate the sample temperature. By adjusting the flow rate of the nitrogen stream, EPR readings could be obtained between 4 K and room temperature.

4.4. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis Ultra DLD spectrometer with monochromatic Al Kα radiation (1486.6 eV). The spectrometer was operated at 1 · 10⁻⁹ Torr base pressure. The survey and high energy
resolution spectra were collected from a 700 x 300 μm² spot, with the X-rays irradiating the surface at 54.7° incidence using fixed analyzer pass energies of 160 and 20 eV. The obtained spectra were analyzed using CasaXPS with individual peaks fitted with a Gaussian-Lorentzian function and a Shirley background subtraction. Spectrometer sensitivity factors and photoelectron escape depth variation for the analyzed elements were taken into account with the software analysis.

4.5. Infrared Spectroscopy

Infrared (IR) spectroscopy was performed using a Bruker Alpha-P spectrometer. Powders were deposited on the surface of the instrument platen. A piston was lowered to depress the powders next to the detector and to seal the detector from the ambient environment. The spectrometer was run utilizing Opus 6.5 software. Opus 6.5 allowed for background subtraction and interactive peak picking. Results were exported to Microsoft Excel for graphing and background removal.

4.6. Laser Flash Analysis

Thermal diffusivities were determined by laser flash analysis using a NETZSCH LFA 457 MicroFlash. A powder pressed into pellet form was sanded with 500 grit sandpaper to 5.80 mm x 5.80 mm dimensions. The thickness was recorded with a micrometer and used for internal calculation. The sample was placed in the instrument in a helium environment. A constant thermal expansion coefficient was assumed and used for internal calculation. Thermal diffusivities were evaluated at 25 °C intervals from -25 to 300 °C. Three data points at each temperature interval were recorded and averaged. Results were exported to Microsoft Excel for graphing and numerical interpretation.
4.7. **Modulated Differential Scanning Calorimetry**

Modulated differential scanning calorimetry (MDSC) was performed using a TA Instruments Q1000. Loose powders were weighed and hermetically sealed in aluminum MDSC pans. For PVD, an aluminum pan was placed in the deposition chamber, and 15 bi-layers were formed by depositing C$_{60}$ for 600 seconds and then manganese for 60 seconds, as described later in Chapter 6. The pan was hermetically sealed for testing. For all samples, a ramp rate of 2 °C/min was used. Results were exported to Microsoft Excel for graphing and numerical interpretation.

4.8. **4-Point Probe**

4-point resistance measurements were performed using a Loresta-EP MCP-T360 handheld reader. A Loresta TFP probe was attached to the reader. The four probe tips were separated tip-tip at 1 mm intervals linearly. Resistance measurement were obtained using an RCF factor (a correction factor based on sample geometry) of 3.670 for pressed pellets and 0.990 for thin films. Results were average over as many reading as could be recorded in a one minute interval.

4.9. **Bulk Thermopower**

Bulk thermopower measurements were obtained on a sample prepared by pressing loose powder into a pellet. The pellet was sandwiched between two copper plates in which one was in contact with a hot plate and the other was attached to a coolant loop. The coolant loop was maintained at 15 °C using a NESTLAB RTE 7 chiller while the Corning PC-420D hot plate was slowly stepped up to 300 °C. A 32 gauge T-type micro-thermocouple was imbedded into the center of each copper plate. The thermocouples
were rated to an accuracy of ±0.5 °C and attached to an Omega OM DAQPRO-5300 DAQ. The copper lead of each thermocouple was also wired into an additional DAQ input, thereby allowing the voltage difference between the two thermocouples to be recorded. It was assumed that, due to the copper plates’ high thermal conductivity and low thermopower, the temperature measured was the same at the surface of the pellet; similarly, the voltage recorded was attributed to the carrier behavior of the pellet. The results were exported to Microsoft Excel for graphing and thermopower calculation using Equation 1.

4.10. Potential-Seebeck Microprobe

Thermopower measurements were obtained using a Potential-Seebeck Microprobe (PSM) from LOT-Quantum Design. Thermopower was spatially resolved across the surface of the sample. The technique required substrates to be thermally conductive to ensure heating of the sample over time did not occur. The sample was attached to holder and a heat probe tip traced an array of data points across the sample. The results were exported to Microsoft Excel for numerical analysis. Outlying data attributable to instrument error was excluded. Data was then graphed on a normal distribution plot, and the thermopower results were derived from fitting the data to a normal distribution.

4.11. Time-Domain Thermal Reflectance

Thermal conductivity for a film was determined by time-domain thermal reflectance (TDTR) measurements utilizing a pump probe technique. In order for testing to be conducted, the sample was coated in a thin film (~90 nm) of aluminum. The pump
beam and probe beam were then focused on a \( \sim 50 \, \mu \text{m} \) diameter spot at a 45° angle to the sample. The incident laser powers at the sample position for the pump and probe beams were 100 and 20 mW respectively. Each scan was then individually modeled knowing the sample thickness and heat capacity.
CHAPTER V

WET CHEMICAL SYNTHESIS

5.1. Wet Synthetic Approach

A bulk synthetic method of generating material is crucial to the development of TE materials since typical devices require grams of constituent materials. A redox reaction has been modified to accomplish this goal. A similar synthetic protocol to one which yielded an air stable zinc fulleride was employed in an effort to prepare manganese fulleride. The proposed reaction is:

$$\text{Mn} + 2\text{C}_{60} \rightarrow \text{Mn} + 2\text{C}_{60}$$

(8)

5.2. Original Protocol Experimental

Manganese powder (Sigma-Aldrich, ≥99%, -325 mesh) and granular C₆₀ (MER, 99+) were stored in an argon filled glovebox with less than 0.1 ppm oxygen. A 1 L round bottom flask, rubber septum, and magnetic stir bar were loaded into the glovebox’s antechamber, and the contents were evacuated and purged with argon 3 times. The round bottom flask was then taken into the glovebox where 1.00 g (1.39 mmol) of C₆₀ and 3.21 g (58.4 mmol) of manganese were introduced into the vessel along with the stir bar. Anhydrous and inhibitor free tetrahydrofuran (THF) was added to the reaction vessel to give a total volume of 400 mL. The round bottom flask was sealed with the rubber
septum and transported out of the glovebox to a magnetic stir plate. The stir plate was turned to medium and the mixture was allowed to evenly mix.

Fresh manganese hydroxide was then prepared to be added to the round bottom flask. An aqueous solution of manganese hydroxide was formed from manganese sulfate monohydrate and ammonium hydroxide as shown in Equation 9.

\[
\text{MnSO}_4 \cdot \text{H}_2\text{O} + 2\text{NH}_4\text{OH} \rightarrow \text{Mn(OH)}_2 + (\text{NH}_4)_2\text{SO}_4
\]  

(9)

Manganese sulfate monohydrate, 50.94 g (337.3 mmol), and deionized water, 500 mL, were added to a 600 mL beaker. A magnetic stir bar was added and the solution was mixed thoroughly to ensure manganese sulfate was in solution. Approximately 50% stoichiometric excess ammonium hydroxide, 41.0 mL (1030 mmol), was dispensed into the beaker. The reaction yielded a near instantaneous white precipitate, manganese hydroxide, from the light pink coloring of the manganese sulfate solution.

Simultaneously, a thin brown film formed across the surface of the beaker. The film was attributed to a side reaction forming manganese oxide from the manganese hydroxide in the presence of atmospheric oxygen.

The fresh manganese hydroxide, approximately 30 g (337 mmol), was syringed into the 1 L round bottom flask containing the THF solution. A condensation column was attached to the top of the reaction vessel to minimize solvent loss due to the heat of reaction. The condensation column was sealed with parafilm and a needle was inserted to relieve any hydrogen gas being generated in the reaction. The reaction was allowed to proceed for 1 week at room temperature. The proposed redox reaction illustrated below in Figure 14 and the redox half reaction steps are explained in Appendix A.
Figure 14: Proposed mechanism for the formation of manganese fulleride

After 7 days the product was extracted through vacuum filtration using a medium frit in the open atmosphere. The solution was washed with deionized water followed by a 3 M HCl wash and the mother liquor was discarded. The remaining material in the frit was collected for analysis as manganese fulleride.

5.3. New Protocol Experimental

A new, inert environment, protocol was derived out of concerns from atmospheric oxygen contamination. To achieve this control, a 1 L two neck round bottom flask, needle valve, rubber septum, and magnetic stir bar were loaded into the glovebox’s antechamber and the contents were evacuated and purged with argon 3 times. The round bottom flask was then taken into the glovebox where 1.00 g (1.39 mmol) of C₆₀ and 3.21 g (58.4 mmol) of manganese were introduced into the vessel along with the stir bar. Anhydrous and inhibitor free THF was added to the reaction vessel to give a total volume of 400 mL. The round bottom flask was sealed with the rubber septum and needle valve
and transported out of the glovebox to a magnetic stir plate. The needle valve was attached to an argon line. Argon was bled into the round bottom flask at a low flow rate and a needle was inserted into the septum to relieve the pressure. The stir plate was turned to medium, and the mixture was allowed to evenly mix.

Fresh manganese hydroxide was then prepared anaerobically. To ensure no oxygen was present when preparing the manganese hydroxide and causing a side reaction to form manganese oxide, a series of degassing steps was undertaken. Manganese sulfate monohydrate, 50.94 g (337.3 mmol) and a stir bar were added to a 1 L three neck round bottom flask. The flask was sealed with a needle valve and rubber septae, then evacuated and purged 3 times with argon on a Schlenk line. Argon was then bled into the flask at a low flow rate and a needle inserted into a septum to relieve pressure. In a second round bottom flask, 500 mL of deionized water was sealed with a septum. The water was degassed by argon bubbling for 20 minutes prior to being syringed into the manganese sulfate. The solution was mixed thoroughly.

The flow rate of argon into the aqueous manganese sulfate was increased and one of the septae removed. The septum was replaced with an addition funnel and sealed with parafilm. The needle was moved to penetrate the parafilm and the argon flow rate was decreased after 20 minutes. In a third round bottom flask, 50 mL of ammonium hydroxide was sealed with parafilm. Due to ammonium hydroxide’s reactivity with metals, the solution was degassed by argon bubbling using a glass pipet. After 20 minutes, the ammonium hydroxide was pipetted into the addition funnel. Once all the ammonium hydroxide was transferred, the stopcock was opened allowing the ammonium hydroxide to react with the manganese sulfate. The stopcock was closed after 41.0 mL
(1030 mmol) was dispensed, approximately 50% stoichiometric excess. The reaction yielded a near instantaneous white precipitate; however, the solution was allowed to continue stirring for an additional 5 minutes to ensure all the manganese sulfate had formed manganese hydroxide. No brown film formation was observed.

The fresh manganese hydroxide, approximately 30 g (337 mmol), was syringed into the 1 L round bottom flask containing the THF solution. The flow rate of argon was increased as the rubber septum was removed and replaced with a condensation column. The condensation column was attached to the top of the reaction vessel to minimize solvent loss due to the heat of reaction. The condensation column was sealed with a needle valve to act as a relief for the argon and any hydrogen gas being generated in the reaction. The reaction was allowed to proceed for 1 week at room temperature.

After 7 days the product was extracted through vacuum filtration using a course frit in the open atmosphere. The solution was washed with deionized water and the mother liquor was discarded. The remaining contents in the frit were then washed with a 3 M HCl wash until the filtrate was clear. The filtrate was run through a fine frit, due to cloudiness of the filtrate, and the resulting filtrate was rotary evaporated to dryness. The resulting powder was confirmed to be MnCl₂ based on EDS. The contents remaining on the course and fine frits were combined in a vial and dried in vacuo.

5.3.1. Blank Reactions

A series of blank reactions was performed to check for unforeseen side reactions. Two half scale blank reactions were set up such that one contained manganese and manganese hydroxide and the other contained C₆₀ and manganese hydroxide. The reactions were set up identical to the new protocol (Section 5.3) and allowed to react for
7 days. In both cases the reaction mixtures were filtered through fine frits and precipitates washed with liberal amounts of deionized water. A 3 M HCl wash removed unreacted manganese hydroxide and the remaining contents were examined. The manganese blank reaction (containing no C$_{60}$) showed no reaction as only manganese mesh remained. The C$_{60}$ blank reaction (containing no manganese mesh) generated a similar brown powder to the original and new protocol powders. The contents of the C$_{60}$ blank reaction were stored and analyzed along with the original and new protocol powders collected.
CHAPTER VI

WET CHEMICAL SYNTHESIS RESULTS AND DISCUSSION

The newly formed manganese-fullerene product was examined using multiple techniques to ensure the fullerene cage was intact and to determine the stoichiometry. Further studies were conducted to examine the material properties.

6.1. Structure and Stoichiometry

Morphology of the loose powders was examined using SEM according to Section 4.1, and images were taken of the material at random locations to examine sample homogeneity. A representative image is shown in Figure 15. Small aggregates clustered together were seen across all samples. As a result, it was concluded that all samples were homogeneous.
Figure 15: Representative SEM image of manganese fulleride powder. Material shown is original protocol manganese fulleride.

It was observed while imaging the samples that charging was occurring on the sample surfaces. This was the result of a buildup of excess electrons due to the electron’s inability to reach the sample holder which was grounded. This is a common issue associated with non-conductive samples.\textsuperscript{70} Charging was present for all fulleride samples with the most aggressive being the new protocol’s manganese fulleride. Figure 16 illustrates the charging effects occurring on samples. Electron build up occurred on large clusters of fulleride rather than finer powder adhered to the carbon dot. This suggests that the bulk manganese fulleride, while resistive, is still able to transfer electrons in thin layers.
Elemental analysis was performed initially with EDS to determine the relative ratios of manganese to C$_{60}$. Unfortunately, to observe the manganese, the detector power was great enough to probe into the carbon dot holding the material, thereby skewing the relative carbon content. Nevertheless, the dispersive pattern revealed the original powder contained oxygen, sulfur, and chlorine along with manganese and carbon. The source of these additional elements will be explained (*vide infra*).

Raman spectroscopy was performed on the powders to ensure the C$_{60}$ cage was intact. C$_{60}$ has a unique Raman spectrum due to the multiple vibrational modes present at room temperature. These Raman active modes include: $H_g(1)$ through $H_g(8)$ and $A_g(1)$ and $A_g(2)$ where $H_g$ modes are fivefold degenerate and $A_g$ modes are singly degenerate, see Figure 17.\textsuperscript{71}
Raman spectroscopy was also insightful due to a correlation published by Talyzin et al. which relates the degree of downshifting of the $A_g(2)$ mode to the number of electrons on the $C_{60}$ cage. The $A_g(2)$ mode is attributed to molecular breathing of the $C_{60}$ cage through pentagonal ring expansion and contraction. On neutral $C_{60}$, the expansions and contractions are uniform across all bonds; however, the addition of electrons on the cage disrupts the symmetry and subsequently alters the spectra. An empirical correlation has been proposed relating every 6 cm$^{-1}$ shift of the $A_g(2)$ mode downfield from 1468 cm$^{-1}$ (observed for neutral $C_{60}$) per each electron added to the $C_{60}$ cage.$^{68,72,73}$

Raman spectra of the loose powder were obtained, see Figure 18 and Appendix B. From the figure, it can be observed the $C_{60}$ structure remained after all reactions;
however, there were slight variations to the spectra. A reduction in the relative intensity of the $A_g(2)$ mode was present for all powders compared to the stock $C_{60}$.

It can also be observed that the $A_g(2)$ mode exhibits a shoulder on the low energy side of the peak. Peak deconvolution was performed and subpeak locations were analyzed, see Figure 19. Subpeaks were observed at $\sim 1468$ cm$^{-1}$ and $\sim 1462$ cm$^{-1}$ for the loose powders. This is suggestive of one electron present on the cage of some of the $C_{60}$, and the presence of neutral $C_{60}$. Relative ratios of charged and neutral $C_{60}$ can be determined assuming the area under each curve is proportional to the species concentration. The original protocol powder had a 3:2 ratio of $C_{60}^{1-}$ to $C_{60}^{0}$ whereas the new protocol powder exhibited a ratio closer to 1:1. Interestingly, the $C_{60}$ blank reaction (manganese hydroxide, no manganese) showed a ratio of 4:1 in favor of the charged $C_{60}$ complex. This is suggestive that the blank reaction was also generated a fulleride structure as well.
Figure 18: Raman spectrum for stock C\textsubscript{60} (bottom, blue), original protocol powder (red), new protocol powder (green), and C\textsubscript{60} blank reaction powder (top, purple).

Figure 19: Peak fitting of the Raman A\textsubscript{g}(2) mode for (a) stock C\textsubscript{60}, (b) original protocol powder, (c) new protocol powder, and (d) C\textsubscript{60} blank reaction powder.
EPR spectroscopy was employed to examine the spins in the manganese fulleride powders. Unlike the empirical correlation from Raman, EPR is a technique for the direct study of unpaired electrons. The proposed reaction (Equation 8) would generate the EPR observable \( C_{60}^1 \) ion.

The EPR spectra were recorded of the manganese fulleride at decreasing temperatures to allow for greater clarity of signal location and probe for temperature effects. It was observed for the new protocol and \( C_{60} \) blank reactions that a single, sharp signal existed and the signal was not strongly temperature dependent, see Figure 20 (a) and (b). The original protocol powder showed a similar signal along with a broad signal centered at the same location that showed temperature sensitivity, see Figure 21. Using Equation 10 the electron’s g-factor can be determined by knowing the magnetic field strength and the microwave frequency.

\[
\Delta E = h \cdot v = g \cdot \mu_B \cdot B_0
\]  

(10)

Based on the literature, the sharp signal at \( X = \sim 3354 \) gauss (g-value = 2.001) with a linewidth of \( \sim 3 \) gauss was attributed to a \( C_{60} \) impurity, \( C_{120}O \), created when \( C_{60} \) was exposed to oxygen. An EPR spectrum of stock \( C_{60} \) was obtained, see Figure 20c. Since \( C_{60} \) contains no free electrons, the EPR spectrum was expected to be silent. A signal appeared in the spectrum attributable to \( C_{120}O \); therefore, the signal in the powders was attributed to \( C_{120}O \) and it existed prior to any reactions and was not a result of redox chemistry.

The absence of a broad signal for the new protocol powder could be the result of even further reduction of \( C_{60} \). The literature reports that \( C_{60}^{2-} \) ion is EPR silent. The silent nature is believed to be due to a Jahn-Teller distortion induced electron pairing. A
simple Jahn-Teller analysis would predict a spin triplet with two unpaired electrons; however, as reported in the literature, it is more favorable to pair electrons in the triplet which might appear as a violation to Hund’s Rule. As a consequence, the $\text{C}_{60}^{2-}$ ion would be a diamagnetic anion and EPR silent. Furthermore, since the $\text{C}_{60}$ blank reaction powder gave no signal other than $\text{C}_{120}\text{O}$, the powder may also contain the $\text{C}_{60}^{2-}$ ion.
Figure 20: EPR spectrum at room temperature for (a) new protocol powder, (b) C60 blank reaction powder, and (c) stock C60.
The EPR for the original protocol powder, shown in Figure 21, exhibited three resonance responses. The sharp signal centered at ~3353 gauss (g-value = 2.001), was attributed to the C_{120}O impurity. The second response was a broad signal centered at approximately the same location and was believed to be a charged C_{60}^{n-} species. From literature, C_{60}^{1-} and C_{60}^{3-} are EPR active and have broad signals located at g-values of ~2.000. Also, the literature states that C_{60}^{1-} and C_{60}^{3-} are temperature sensitive\(^75,76\). Therefore, it was concluded that the original protocol powder contains C_{60}^{1-} paramagnetic ions due the g-value and the temperature sensitive broad signal. However, the literature C_{60}^{1-} linewidth was reported to be upwards of 87 gauss at 200 K,\(^76\) whereas the original

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure21.png}
\caption{EPR spectrum for original protocol powder with respect to temperature.}
\end{figure}

The EPR for the original protocol powder, shown in Figure 21, exhibited three resonance responses. The sharp signal centered at ~3353 gauss (g-value = 2.001), was attributed to the C_{120}O impurity. The second response was a broad signal centered at approximately the same location and was believed to be a charged C_{60}^{n-} species. From literature, C_{60}^{1-} and C_{60}^{3-} are EPR active and have broad signals located at g-values of ~2.000. Also, the literature states that C_{60}^{1-} and C_{60}^{3-} are temperature sensitive\(^75,76\). Therefore, it was concluded that the original protocol powder contains C_{60}^{1-} paramagnetic ions due the g-value and the temperature sensitive broad signal. However, the literature C_{60}^{1-} linewidth was reported to be upwards of 87 gauss at 200 K,\(^76\) whereas the original
protocol powder’s linewidth at room temperature was 200 gauss and grew to 500 gauss at 4 K. The increase in linewidth is consistent with that observed in a polycrystalline powder which is attributed to the local environment heterogeneity associated with the EPR active species.77

A third response was a shoulder at ~2640 gauss that became more noticeable as temperature decreased. The source of the shoulder was eventually concluded to be the result a fullerol product (vide infra). The shoulder was similar to literature results except at above room temperature, the shoulder and main peak merged whereas, the original protocol powder’s shoulder was obscured due to the size of the main peak.78

Elemental compositions were determined using XPS according to Section 4.4. By utilizing this technique, only the uppermost atomic layers are examined. XPS avoids the problem of penetration to the adhesive carbon layer associated with EDS. The results are normalized with respect to manganese and tabulated along with the atomic percentages in Table 2 through Table 4.

### Table 2: XPS results of original protocol powder

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn 2p</td>
<td>639</td>
<td>0.45</td>
<td>1</td>
</tr>
<tr>
<td>C 1s</td>
<td>282</td>
<td>85.85</td>
<td>190.8</td>
</tr>
<tr>
<td>N 1s</td>
<td>396.5</td>
<td>1.01</td>
<td>2.2</td>
</tr>
<tr>
<td>O 1s</td>
<td>529.5</td>
<td>11.46</td>
<td>25.5</td>
</tr>
<tr>
<td>S 2p</td>
<td>166</td>
<td>0.57</td>
<td>1.3</td>
</tr>
<tr>
<td>Cl 2p</td>
<td>197</td>
<td>0.66</td>
<td>1.5</td>
</tr>
</tbody>
</table>
The samples, as with the EDS results, contained elements other than manganese and carbon. The extraneous element that raises the most concern is oxygen. The atomic percentage of oxygen is very high. Some oxygen can be attributed to C\textsubscript{120}O and SiO\textsubscript{2}, see Table 5. In the previous work for the analogous wet chemical synthesis of zinc fulleride, it was found that some THF was incorporated into the product. However the low hydrogen percentage, *vide infra*, rules out any significant contribution.
The new protocol powder, which contained the highest oxygen content according to XPS, was sent to Galbraith Laboratories for chemical elemental analysis. The results are tabulated in Table 6.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Mass Conc. [%]</th>
<th>Ratio of Atomic Conc. to Mn Atomic Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese</td>
<td>0.443%</td>
<td>1</td>
</tr>
<tr>
<td>Carbon</td>
<td>83.22%</td>
<td>859.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>&lt;0.5%</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.73%</td>
<td>21.2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.140%</td>
<td>0.5</td>
</tr>
<tr>
<td>Chloride, non-aqueous</td>
<td>0.746%</td>
<td>2.7</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>&lt;0.5%</td>
<td></td>
</tr>
<tr>
<td>Unknown</td>
<td>11.721 – 12.721</td>
<td></td>
</tr>
</tbody>
</table>

The XPS results showed an oxygen to manganese ratio of ~29.6:1 for both the new protocol and C₆₀ blank reactions, and a 25.5:1 ratio for the original protocol powder. The Galbraith results were a 21.2:1 ratio for the new protocol product. Assuming all the manganese present were MnO₄⁻, the highest possible oxidation state (unlikely to form due to the reducing conditions present), this would still not adequately account for the oxygen content. Thereby, it must be concluded that there is some interaction between oxygen and C₆₀. Moreover, this interaction cannot be solely attributed to C₁₂₀O, known to exist in the product, as there still remains too much oxygen. The oxygen to manganese ratio of the original protocol as determined by EDS was 11.3:1, which is significantly different than XPS. EDS was performed soon after synthesis, whereas the XPS and Galbraith techniques were performed over a month later.

It was concluded that all the carbon present was attributed to C₆₀ species based on the Raman results. It is insightful to examine the ratios between manganese and C₆₀. The C₆₀ to manganese ratio for the original and new protocol according to XPS were ~3.0:1
whereas the C₆₀ blank reaction was 5.5:1. Similarly, the binding energy for the manganese was higher for the C₆₀ blank reaction than the other protocols, indicating the manganese may have a different charge state. However, the Galbraith C₆₀ to manganese ratio was 14.3:1 for the new protocol powder, almost 5x greater than the XPS result. It was concluded that the higher ratio was a result of unreacted C₆₀. The reacted fulleride species exist at the surface, whereas unreacted fullerene resides inside the aggregate.

The elemental results are inconclusive as to the stoichiometry of the manganese fulleride. Also, due to high oxygen content in all samples, concern about the air stability of the products is raised.

IR spectroscopy was performed to determine the nature of the carbon and oxygen bonding. IR spectra were recorded for the powder shown in Figure 22 and peak locations are tabulated in Appendix C.
From the IR spectra, a small band was observed between 3500 and 3200 cm\(^{-1}\) for all reactions products. This corresponded with O-H bonding; however the peaks was not as intense as often observed for hydroxyl groups. Fullerols, hydroxylated \(C_60\) molecules, have been reported and their IR compared with present results. Fullerols, hydroxylated \(C_60\) molecules, have been reported and their IR compared with present results.\(^79\) In the fingerprint region below 1500 cm\(^{-1}\), peaks at ~1062, ~1375, and ~1625 cm\(^{-1}\) indicate fullerol presence along with neutral \(C_{60}\).

Fullerols have been reported to contain up to 26 hydroxyl groups which rendered them water soluble. Also, it was reported that anaerobic hydroxylation occurs, albeit slower than under atmospheric conditions. The IR results in Figure 22 indicate that anaerobic hydroxylation occurred in all reactions. The relative intensity in the IR...
indicated that a greater degree of hydroxylation occurred in the original protocol, which is consistent with the less stringent reaction conditions. Lastly, the IR results confirmed that the C$_{60}$ blank reaction was not a non-reactive system and hydroxyl groups did bind with the C$_{60}$ cage.

6.2. Transport Properties

The loose powders were analyzed for the key TE properties: thermal conductivity, thermopower, and electrical conductivity. However, the limited amount of material available for testing requires some assumptions to be made concerning some of the powders.

Thermal conductivity was determined using Equation 11. Unfortunately testing required large amounts of powders and only the original protocol could be evaluated for thermal conductivity. However, it is a reasonable assumption that all powders will have on the same order of magnitude thermal conductivities.

\[
\kappa = C_p \cdot \rho \cdot \alpha
\]  

(11)

The heat capacity was found using MDSC from -25 to 500 °C, see Appendix D. The original protocol powder was pressed into pellet form for further testing. A pellet was fabricated in a 10 mm diameter pellet press from Across International at 10 MPa for 15 minutes. The pellet was removed from the pressing die; however, the pellet fractured and broke along the fracture planes into four disks, see Figure 23. This raised concerns about mechanical integrity.
Density was determined from one of the fractured pellets by weighing the pellet and finding it’s displacement in water. The density was determined to be 1282 kg/m³ (assuming the pellet is 90% packing efficiency) and assumed to be independent of temperature (i.e. minimal thermal expansion). This is lower than 1650 kg/m³, the density for crystalline C₆₀. The decrease in density is consistent with decreased packing efficiency expected to be a result of hydroxyl groups attached to the C₆₀. The cages cannot pack as tightly due to the steric hindrance and thereby decrease the density as the lattice framework increases.

Thermal diffusivity was found using laser flash analysis from -25 to 300 °C, see Appendix D. Utilizing Equation 11, the thermal conductivity was determined, see Figure 24. From the figure, the thermal conductivity was determined to be not strongly correlated with temperature in the -50 to 300 °C temperature range. The thermal conductivity varied between 0.15 and 0.28 W/(m · K) which agreed well with previously obtained results on zinc fulleride. Due to the similar thermal conductivities, the assumption that the untested new protocol and C₆₀ blank reaction powders have similar thermal conductivity as the original protocol was kept. The thermal conductivity range for the sample is half crystalline C₆₀’s thermal conductivity.
Figure 24: Thermal conductivity of original protocol powder

The electrical conductivity was determined on the same sample utilized in thermal diffusivity measurements by using a 4 point probe technique as outlined in Section 4.8. The electrical conductivity obtained was $4.4 \cdot 10^{-2} \, 1/(\Omega \cdot \text{m})$. Unfortunately, this electrical conductivity value is too resistive for a TE devices as it is more desirable to have electrical conductivities on the order of $10^5 \, 1/(\Omega \cdot \text{m})$. The resistive nature had been suspected after observing the charging on SEM samples. It is assumed that the new protocol and C_{60} blank reaction products have low electrical conductivities since they also exhibited charging during SEM analysis; however, limited sample availability precluded sample measurement on those materials.

The remaining key TE property was the thermopower. Again only the original protocol powder was examined as a pressed pellet was required. The homebuilt
apparatus as described in Section 4.9 was used for thermopower analysis. While the apparatus provided good results for reference materials, no thermopower could be observed for the original protocol pressed pellet. This was believed to be the result of the resistive nature of the powder and is consistent with a material with a high bandgap or a material with multiple resistive interfaces.
CHAPTER VII

THIN FILM DEPOSITION

7.1. Thin Film Approach

The semi-conductive properties of TE materials are strongly dependent upon composition and doping levels. Given the limitless stoichiometric ratios that can be formed between multiple materials, finding the ideal ratio for optimal TE performance at a given temperature can be daunting. A thin film depositional approach was pursued in order to reduce the search time. The PVD approach consisted of using magnetron sputtering and thermal evaporation to form alternating nanometer thick layers of manganese and C$_{60}$ respectively.

7.2. Deposition Chamber

PVD technology allows for atomic films to be deposited onto a substrate in a clean, ultra-low vacuum environment. The deposition chamber used for PVD in the present work had previously been used for zinc fulleride depositions. The main components used in the chamber can be seen in Figure 25.
Figure 25: Physical vapor deposition chamber with major components. Magnetron (purple), manganese target (brown), thermal evaporator holder (dark blue), thermal evaporator (light blue), tungsten wire (black lines on thermal evaporator), C\textsubscript{60} (gray), sample stage (dark green), sample holder (light green), and sample (red).

The PVD chamber used consisted of a stainless steel sphere with numerous inlet ports. The most important device attached to a port was the Varian Turbo-V 550 main turbo pump. The turbo pump maintained the ultra-low vacuum needed in the system and was cooled by a chiller flow loop maintained at 25 °C. The turbo pump operated at a constant 42 kRPM and maintained a base pressure in the chamber on the order of 10\textsuperscript{-6} to 10\textsuperscript{-8} Torr. During chamber operation, the turbo pump required ~168 W, up from an idle ~25 W, to maintain the fan revolution speed. A roughing pump was attached in line after the turbo pump to remove the gaseous molecules the turbo pump exhausted from the
chamber. The roughing pump operated on the order of $10^{-2}$ Torr and $10^{-1}$ Torr when the system was in use.

A second major component used in the deposition process was the side antechamber. The antechamber allowed samples to be moved in and out of the system while under deep vacuum. The antechamber was attached to the main chamber by a vacuum grade gate valve. The pressure inside the antechamber was maintained by the roughing pump and a smaller Leybold TURBOVAC 50 turbo pump. A second gate valve just after the turbo pump separated the antechamber from the roughing pump. Consequently, the antechamber could be closed off and completely isolated from the larger deposition system. A hinged door and up-to-air valve were attached to the antechamber. Samples were inserted while at atmospheric pressure, and after sealing the system, the antechamber could be lowered to approximately the main chamber’s pressure.

Moving samples from the antechamber to the main chamber required a sample holder and transfer-arm. Samples were attached to the sample holder, see Figure 26, with double sided tape. This ensured the samples would not fall off during any movement inside the chamber or due to sudden pressure differences. The lower lip of the sample holder was then inserted between the two tongs of the transfer arm. When system pressures were approximately equal, the gate valve between the antechamber and the main chamber was opened. The transfer arm was moved with a magnet into the chamber where the sample holder rested on the sample stage. This transfer technique required no gasket or seal which could leak atmospheric gases into the system.
Inside the PVD chamber, the sample holder’s bottom edge rested inside a cup on the sample stage. This ensured the sample holder remained in a constant location for every deposition. The sample stage was attached to a translational stage that allowed the sample stage to be raised (to load and unload the sample holder) and lowered (to perform PVD depositions). To ensure even film deposition, the cup in which the sample holder rested was rotated. It had previously been determined that rotating at ~36 RPM allowed for even films to be grown. An Advanced Energy MDX-1K DC power supply was attached to the sample stage to allow for biasing of the sample holder. Voltage could be manipulated from 0 V to 800 V where 800 V allowed for an argon etching process to remove monolayers off of a substrate.

With the sample in the chamber, the PVD process was performed. A Legacy US Gun 1.3” standard balanced magnetron was used for film growth. A manganese target (Plasmaterials, 99.95% pure, 1.3” dia x 0.25” thickness) was attached to the magnetron. It was later determined that the manganese target was too thick, so the target was reduced to 0.125” thickness. The magnetron was powered by a second Advanced Energy MDX-1K DC power supply at 15 W. The chamber pressure was set to 15 mTorr for magnetron sputtering. To obtain the desired pressure for experiments, a MKS Multi Gas Controller

Figure 26: Sample holder, (left) side view and (right) top view.
647C was used to flow 50 SCCM of argon into the main chamber by the attached argon line. A MKS 600 Series Pressure PID controller regulated the pressure by adjusting a butterfly valve located in front of the turbo pump.

The second source for PVD film growth was a thermal evaporator. The thermal evaporator deposited C$_{60}$ through sublimation. The evaporator, see Figure 27, was a modified crucible design made of the ceramic Macor. A tungsten wire wrapping around the outside of the evaporator was heated using an Agilent 6033A System Power Supply. A ramping cycle of stepping the power through the wire at 10 W for 10 minutes followed by 15 W for 20 minutes and lastly 20 W for 30 had previously been determined to heat the thermal evaporator to an appropriate temperature for C$_{60}$ sublimation. C$_{60}$ (MER, 99%+) was stored inside the crucible in the donut shaped cavity. The top of the thermal evaporator was covered by the thermal evaporator holder; thereby only allowing C$_{60}$ to deposit from the central hole in the bottom. It had already been determined that upon completion of the temperature ramp cycle, the plume of C$_{60}$ leaving the thermal evaporator was quasi-steady state in nature. As C$_{60}$ was being continually deposited once the thermal evaporator was heated, a shutter was located below the thermal evaporator to block its deposition to the sample as required. The shutter was pneumatically controlled by an electrically controlled relay.

![Figure 27: Thermal evaporator, (left) side cutaway and (right) top view.](image)
The magnetron, thermal evaporator shutter, and sample biasing were computer controlled. Consequently, depositions were run semi-automatically once a code was input.

### 7.2.1. Sample Preparation

P-doped silicon wafers (Virginia Semiconductor, 1” dia x 265 μm) with a resistivity of 1-10 Ω·cm were scored and cleaved into quarters. One quarter of the wafer was placed into an ultrasonic bath for cleaning. Excess wafers were stored in sample holders for later depositions. The working fluid, acetone, was added to the ultrasonic bath and the sample was cleaned for 30 minutes. The sample was removed from the bath and wiped gently with a Kimwipe to remove acetone and any residue. The sample was affixed to the sample holder and loaded into the side antechamber for PVD film growth.

A copper substrate (commercially available copper, 15 mm x 20 mm x 0.32 mm) was polished to a mirror-like surface. A similar polishing technique adopted from pool boiling studies was utilized where surface roughness was maintained below 14 nm ± 2.0 nm. The 0.32 mm thick copper substrate was first polished with 400 grit sandpaper on a polishing wheel in a “figure 8” pattern. The copper substrate was then polished with an 800 grit silicon carbide sandpaper until uniform roughness. The third step required a lapping procedure using a Gold Label polishing cloth and a 9 μm polycrystalline diamond paste. Lastly, all of the visible scratches on the substrate were polished off with a Microcloth polishing cloth and 1 μm polycrystalline diamond paste. The copper substrate was placed in an ultra-sonic bath with acetone as the working fluid for 30 minutes. The sample was then transferred to the deposition chamber for the last cleaning/preparation step. Argon etching was performed in a 40 mTorr argon atmosphere with the sample stage biased at 800 V for 1
hour. The biasing was then removed and the pressure lowered to 15 mTorr as the sample was ready for PVD film growth.

7.2.2. PVD Film Growth Rate

Before samples were grown for analysis and characterization, the deposition rate for each PVD source was determined. Silicon wafers were used as sample substrates for deposition. A small piece of kapton tape (~2 mm x ~5 mm) was adhered to the edge of the sample with the majority of the tape on the sample. The PVD growth rates for each source are shown in Table 7.

<table>
<thead>
<tr>
<th>Material</th>
<th>Length of Deposition [s]</th>
<th>Average Film Thickness [nm]</th>
<th>PVD Film Growth Rate [nm/s]</th>
<th>PVD Film Growth Rate [mol/(area · s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese</td>
<td>1800</td>
<td>25</td>
<td>$1.4 \cdot 10^{-2}$</td>
<td>$1.9 \cdot 10^{-24}$</td>
</tr>
<tr>
<td>$C_{60}$</td>
<td>12600</td>
<td>43</td>
<td>$3.4 \cdot 10^{-2}$</td>
<td>$7.8 \cdot 10^{-27}$</td>
</tr>
</tbody>
</table>

The film thickness was determined using a KLA Tencor P15 profilometer. To determine the film thickness, the kapton tape was removed from the sample surface to reveal the surface of the silicon. Using the profilometer, the step from the sample surface to the top of the film was determined at six points around the location the kapton tape had been. The average thickness was reported in Table 7. The film thickness was converted to a molar basis using Equation 12.

$$\text{Rate} \left[ \frac{\text{mol}}{\text{area} \cdot \text{s}} \right] = \text{Rate} \left[ \frac{\text{nm}}{\text{s}} \right] \cdot \frac{\rho}{\text{MW}}$$ (12)

The densities for the films were taken from literature. The densities for manganese and $C_{60}$ used were 7470 kg/m³ and 1650 kg/m³, respectively.⁸⁰,⁸³ The molecular deposition rate determined was only used as an approximation and used for determining the
experimental runs. Exact stoichiometries were determined for each experiment using EDS.

7.3. Experimental

A silicon wafer prepared according to Section 7.2.1 was affixed to the center of the sample holder using double sided tape. The sample holder was placed in the side antechamber and vacuum was drawn on the chamber using the roughing pump. The pressure in the antechamber was reduced to $\sim 10^{-2}$ Torr. The side turbo pump was engaged at $5.0 \cdot 10^{-2}$ Torr. The side antechamber did not have a pressure indicator (the previous pressure measurements were from a sensor associated to the roughing pump), so the side antechamber was considered approximately at deep vacuum when the side turbo pump reach operational speed. At operational speed the magnitude of pressure difference was considered to be negligible between the main chamber and side antechamber.

The gate valve separating the antechamber and main chamber was opened. The sample holder was moved to the main chamber and the gate valve closed. The sample stage was lowered in the PVD chamber to the deposition height. The deposition height was constant throughout all experiments and had previously been determined to be the optimum location for PVD film growth. The sample holder rotation was engaged at $\sim 36$ RPM. Argon was introduced into the main chamber at 50 SCCM and the pressure in the chamber was set to 15 mTorr. The thermal evaporator was ramped up to deposition levels using a 10-15-20 W ramp cycle at 10, 20, and 30 minute intervals respectively. This concluded the physical changes to the chamber and attention was focused on the computer terminal.
The computer terminal was programmed to perform the manganese and C₆₀ PVD film growth. A constant bias of 50 V was maintained on the sample holder. This had already been determined to provide better quality films than not biasing or using a higher voltage for biasing. For any given sample number, the deposition sources were alternated starting with C₆₀, see Figure 28. Manganese was then deposited at a power setting of 15 W. The deposition times and desired number of each constituent layer is outlined below in Table 8. The number of layers was manipulated to allow for a constant quantity of C₆₀ deposited among all samples (9000 s or 2.5 hr).

![Sample structure showing layering of constituent materials](image)

**Figure 28: Sample structure showing layering of constituent materials**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Length of C₆₀ Deposition [s]</th>
<th>Length of Manganese Deposition [s]</th>
<th>Number of Each Constituent Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>600</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>600</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>8</td>
<td>200</td>
<td>60</td>
<td>45</td>
</tr>
</tbody>
</table>

After the PVD film was grown, the thermal evaporator was quickly ramped down to 0 W and turned off. The argon flow rate was reduced to 0 SCCM and the pressure controller turned off. The chamber returned to deep vacuum in several minutes. The side antechamber was pumped down to deep vacuum and the gate valve separating the two
systems was opened. The sample stage was raised and the sample holder rotation was turned off. The transfer arm removed the sample holder, and the gate valve was closed. The side antechamber was returned to atmospheric pressure by slowly bleeding in atmosphere after the side turbo pump was turned off and had stopped spinning. The sample holder was removed and the sample placed into a plastic sample contain for analysis.
CHAPTER VIII
THIN FILM DEPOSITION RESULTS AND DISCUSSION

PVD thin films were analyzed to determine the structure and binding nature of the constituent layers. Further studies were conducted to examine the film properties.

8.1. Structure and Stoichiometry

MDSC was employed to determine whether samples required annealing before beginning analysis and characterization. Annealing was used in the analogous zinc fulleride PVD film. The zinc fulleride film exhibited a sharp endotherm at ~357 °C, whereas the manganese fulleride film was observed to have a smaller, broad endotherm at ~370 °C, see Figure 29. In the case of zinc, the endotherm was attributed to zinc diffusing/reacting inside the C\textsubscript{60} framework. Since manganese fulleride thin films also contained a similar endotherm, it was concluded that manganese could become mobile; however, the degree of mobility is greatly diminished compared to zinc. This was to be expected as manganese’s melting point is 1246 °C, whereas zinc’s melting point is 420 °C. Consequently, it was concluded that annealing was required. However, the length of annealing would have to be increased compared to the zinc (12 hr). Annealing was performed at 410 °C (same as zinc fulleride) for four times longer (48 hr) in a tube furnace under flow of pure argon.
Figure 29: MDSC of sample 1 deposition parameters

The evenness of the thin films was examined by SEM. Samples were examined for grain boundary formation or other irregularities. A representative SEM image was shown in Figure 30. It was observed that prior to annealing the samples appeared uniform with the exception of an occasional impurity aggregate on the surface of the film. Prior to annealing, samples were a variety of colors including amber, blue, and purple. After annealing, the samples exhibited a color loss and appeared more like the original silicon substrate. Based on SEM, the aggregates remained on the surface of the films and increased in size, as seen in Figure 30. The aggregates were determined by EDS to be metal clusters, vide infra. However, the surface appeared to no longer be smooth. A slight roughening was observed across the film.
Figure 30: Representative SEM image of manganese fulleride thin films. Films shown are sample 8 (top) prior to annealing and (bottom) after annealing.
Elemental compositions were determined using EDS according to Section 4.1 for the PVD films. EDS scanning power resulted in scanning into the silicon substrate, conveniently, these silicon percentages are ignored as they were not a part of the system. The EDS results are tabulated for films prior to annealing in Table 9.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn Atomic %</th>
<th>C Atomic %</th>
<th>Si Atomic %</th>
<th>O Atomic %</th>
<th>Sn Atomic %</th>
</tr>
</thead>
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<tr>
<td>Sample 1</td>
<td>0.17</td>
<td>65.63</td>
<td>32.14</td>
<td>2.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.15</td>
<td>53.84</td>
<td>36.79</td>
<td>8.16</td>
<td>0.07</td>
</tr>
<tr>
<td>Sample 3</td>
<td>2.32</td>
<td>51.57</td>
<td>29.05</td>
<td>17.07</td>
<td>-</td>
</tr>
<tr>
<td>Sample 4</td>
<td>0.03</td>
<td>65.14</td>
<td>33.61</td>
<td>1.23</td>
<td>-</td>
</tr>
<tr>
<td>Sample 5</td>
<td>0.02</td>
<td>56.87</td>
<td>42.19</td>
<td>0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>Sample 6</td>
<td>0.01</td>
<td>53.02</td>
<td>46.23</td>
<td>0.65</td>
<td>0.09</td>
</tr>
<tr>
<td>Sample 7</td>
<td>0.01</td>
<td>66.93</td>
<td>32.55</td>
<td>0.46</td>
<td>0.06</td>
</tr>
<tr>
<td>Sample 8</td>
<td>1.27</td>
<td>52.81</td>
<td>35.67</td>
<td>10.19</td>
<td>0.07</td>
</tr>
</tbody>
</table>

From the table the extraneous elements, tin and oxygen, were observed in the films prior to annealing. Tin is attributed to the adhesive backing of the manganese target used in deposition and should remain in trace amounts. Oxygen, on the other hand, displays a positive correlation with manganese concentration in samples prior to annealing.

Annealing the samples resulted in a devastating loss of carbon. The loss of carbon was suspected when the samples lost color, but EDS confirmed the hypothesis. There was also a slight reduction in oxygen; however the positive correlation between manganese and oxygen concentration remained. It was concluded that C\textsubscript{60} was able to sublime due the forced convection of argon. This contrasts with work performed prior with the zinc fulleride and is suggestive that the zinc-C\textsubscript{60} lattice is more robust than the manganese-C\textsubscript{60} lattice. It was necessitated analyzing samples without annealing.
Raman spectroscopy was performed to determine if the C\textsubscript{60} cage was intact after sample creation and to determine the nature of any remaining carbon after annealing. The Raman spectra for the samples prior to annealing are shown in Figure 31 and peak information was tabulated in Appendix B. These films were observed to retain many of the C\textsubscript{60} vibrational modes; moreover, with increasing manganese concentration came a strong peak broadening of the higher frequency modes. Simultaneously, dampening of the lower vibrational modes was observed. Similar results were observed for Nb\textsubscript{x}C\textsubscript{60} thin films and previous work with Zn\textsubscript{x}C\textsubscript{60} thin films\textsuperscript{65,67} The A\textsubscript{s}(2) mode in particular exhibited a downshift with increasing manganese until x > 1.4 for Mn\textsubscript{x}C\textsubscript{60}.

Peak deconvolution was performed for the samples prior to annealing and subpeak locations were analyzed similar to Section 6.1. Subpeaks were observed at \textasciitilde 1468 cm\textsuperscript{-1} and \textasciitilde 1462 cm\textsuperscript{-1} for the films. Similar to the conclusion drawn for the loose powders, this is suggestive of one electron present on the cage of some of the C\textsubscript{60}, and the presence of neutral C\textsubscript{60}. Interpreting the area under the curve to be proportional to the C\textsubscript{60} species concentration, a ratio of charged to neutral C\textsubscript{60} can be determined, see Table 10. The sample with the highest \textsubscript{C\textsubscript{60}}\textsuperscript{1-} to \textsubscript{C\textsubscript{60}}\textsuperscript{0} ratio was sample 8 at \textasciitilde 3.2:1 with the next closest being sample 3 at \textasciitilde 2.2:1. The ratio then decreased with decreasing manganese concentration. This trend continued down to sample 7, with a \textsubscript{C\textsubscript{60}}\textsuperscript{1-} to \textsubscript{C\textsubscript{60}}\textsuperscript{0} ratio of 1:3. This is suggestive that all the film created contained some fulleride within them. Reducing the C\textsubscript{60} constituent layer thickness (i.e. samples 2, 3, and 8) resulted in a more intimate layering of the constituent layers and was believed to largely influence the charged to neutral C\textsubscript{60} ratio.
Table 10: Comparison of sample stoichiometry to ratio of charged species present

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$ value for $\text{Mn}<em>x\text{C}</em>{60}$</th>
<th>$\text{C}<em>{60}^{1-}$ to $\text{C}</em>{60}^3$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 8</td>
<td>1.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Sample 3</td>
<td>2.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Sample 1</td>
<td>0.15</td>
<td>1.5</td>
</tr>
<tr>
<td>Sample 5</td>
<td>0.019</td>
<td>0.69</td>
</tr>
<tr>
<td>Sample 4</td>
<td>0.027</td>
<td>0.64</td>
</tr>
<tr>
<td>Sample 6</td>
<td>0.010</td>
<td>0.54</td>
</tr>
<tr>
<td>Sample 7</td>
<td>0.0032</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Samples that were annealed failed to yield any Raman active peaks other than the substrate peak. Subsequently, annealed samples were no longer considered for analysis due to their extremely low carbon content which wasn’t large enough of contribution to be distinguished from noise.

Figure 31: Raman spectra for PVD thin films prior to annealing arranged in decreasing manganese content from sample 3 (lowest) to sample 7 (highest).
Figure 32: Peak fitting of the Raman $A_g(2)$ mode for (a) sample 1 through (h) sample 8 prior to annealing.
8.2. Transport Properties

The PVD films were analyzed for the key TE properties. The electrical conductivity, thermopower, and thermal conductivity were determined on samples that were of greatest interest due to their stoichiometry and the Raman spectra.

The electrical conductivity was measured on samples 1 – 8 prior to and after annealing according to Section 4.8. The samples did not exhibit an electrical conductivity on the silicon wafers. Upon removing the 4-point resistance meter, the samples were observed to have material scratched away from the meter.

A second approach was then taken to measure the film electrical conductivity. As required later for thermopower testing, a film was deposited onto a highly polished copper surface. 4-point resistance testing on the new sample substrate resulted in pin marks on the film, but the material was not scratched or removed during testing. Subsequently, the electrical conductivity was only determined on samples deposited onto copper. Due to material and deposition chamber constraints, only the film of greatest interest was determined; therefore, the electrical conductivity for sample 8’s deposition parameters was determined as it showed the highest $\text{C}_{60}^{1-}$ to $\text{C}_{60}^{0}$ ratio. The electrical conductivity was determined to be $215 \, 1/\text{(Ω m)}$ at room temperature. This compares very well with the 430 $1/(\text{Ω m})$ from the previous zinc fulleride work.\textsuperscript{65} Also, the sample 8 film shows a 4 order of magnitude improvement over the loose powders which were $4.4 \cdot 10^{-2} \, 1/(\text{Ω m})$.

The thermopower of the film on the copper substrate was determined according to Section 4.10. From prior work with the PSM, the copper substrate was required to reject the heat after the heated probe tip left the surface whereas the silicon wafer would heat
over time, skewing the results. The thermopower results were examined on a normal distribution plot, and the resulting thermopower was found to be $9.1 \pm 1.7 \, \mu V/K$ at room temperature. This is similar to thermopowers found in other transition metal fullerides. This value remains too low for effective TE applications.

The thermal conductivity of the PVD film was determined using TDTR which required a previously determined heat capacity from DSC, $\sim 2 \, J/(kg \cdot K)$, and film thickness, $\sim 150 \, nm$. The thermal conductivity of the film was expected to match the analogous zinc fulleride work, $0.15 \, W/(m \cdot K)$ at room temperature. The thermal conductivity was found to be $0.89 \pm 0.02 \, W/(m \cdot K)$. Since the thermal conductivity of the film was on the same order of magnitude as the zinc-fulleride and crystalline C$_{60}$, the thermal conductivity was deemed in very effective for TE application.

Utilizing the room temperature measurements for the key TE properties, a $zT$ can be determined by Equation 6. The $zT$ was found to be $6.0 \cdot 10^{-6}$ at 298 K for Mn$_{1.4}$C$_{60}$. The $zT$ value while low compared to state-of-the-art materials, is nominal for TE materials prior to optimization.
CHAPTER IX

CONCLUSIONS AND FUTURE WORK

Extensive characterization was undertaken to confirm and investigate manganese fulleride(s) produced by two separate approaches. The powders and films produced created a framework through which manganese fulleride was examined for key TE properties.

The loose powders produced through wet chemical synthesis exhibited resistive tendencies during SEM characterization. Powders were observed to contain some downshifting of the Raman $A_g(2)$ mode suggesting some charged species were present. EPR confirmed charged species were present in the original protocol powder, while the spectra were silent for other powders. It was concluded that the majority of species present were not a fulleride, but a fullerol. The analogous reaction with zinc produced a fulleride, so if manganese is still to be considered, reactions that avoid fullerols should be considered for the future. Also an examination of the molecular structure once a manganese fulleride is created should be performed to determine the lattice arrangement.

The key thermoelectric transport properties were examined for the powders. The resulting thermal conductivity was slightly lower than $C_{60}$ itself which can be accounted for by a poor packing efficiency of fullerol derivatives. The electrical conductivity was inhibitive to TE application. Also, the thermopower could not be recorded for the pellet due to the low electrical conductivity.
The PVD films deposited by magnetron sputtering and thermal evaporation were examined as the ratio of manganese was varied. The study illustrated the rapid scanning ability of a covering a wide stoichiometric range. Downshifting of the Raman A_g(2) mode was positively correlated with increasing manganese concentration up to x = 1.4. However, annealing samples under assumed “safe” conditions resulted in the loss of C_60 on the films. A more in-depth examination of annealing is recommended for future studies.

A pre-annealed Mn_{1.4}C_{60} PVD film was examined for key thermoelectric properties. The film was believed to express the most desirable traits from the samples generated. The results revealed the electrical conductivity was 215 1/(Ω·m) and the thermopower was 9.1 μV/K at room temperature. Future studies should focus on more intimate layering of constituent layers and possibly the addition of alloying elements to improve the electrical conductivity and thermopower. Additionally, the electrical conductivity and thermopower should be characterized as functions of manganese content. The thermal conductivity value was 0.89 W/(m·K) at room temperature and believed to not vary significantly as a function of manganese or temperature. The resulting zT for the Mn_{1.4}C_{60} PVD film was 6.0 · 10^{-6} at 298 K. This value is too low for practical use.

It is the opinion of the author that manganese fulleride(s) can only show promise if their electrical and thermoelectric properties increase. While adjusting the Mn_xC_{60} ratio is expected to be fruitful, doping with materials that increase electrical conductivity, i.e. a carrier dense material, needs to be considered.
REFERENCES


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80. The Creative Science Centre. Some Properties of Carbon and \( \text{C}_{60} \).


83. WebElements. Manganese: physical properties.

APPENDIX A

REDUCTION AND OXIDATION HALF STEP REACTIONS

Reduction:

\[ 2C_{60} \rightarrow \text{Mn}(C_{60})_2 \]  \hspace{1cm} (13)

Balance Elements

\[ \text{Mn(OH)}_2 + 2C_{60} \rightarrow \text{Mn}(C_{60})_2 \] \hspace{1cm} (14)

Balance e-

\[ \text{Mn(OH)}_2 + 2C_{60} + 2e^- \rightarrow \text{Mn}(C_{60})_2 \] \hspace{1cm} (15)

Balance charge

\[ \text{Mn(OH)}_2 + 2C_{60} + 2e^- \rightarrow \text{Mn}(C_{60})_2 + 2OH^- \] \hspace{1cm} (16)

Oxidation:

\[ \text{Mn} \rightarrow \text{Mn(OH)}_2 \] \hspace{1cm} (17)

Balance e-

\[ \text{Mn} \rightarrow \text{Mn(OH)}_2 + 2e^- \] \hspace{1cm} (18)

Balance charge

\[ \text{Mn} + 2OH^- \rightarrow \text{Mn(OH)}_2 + 2e^- \] \hspace{1cm} (19)

Combining Equations 16 and 19 yields the proposed Equation 8. For the generation of hydrogen gas mentioned in Section 5.2 and 5.3, the oxidation half reaction remains the same; however, the reduction step is modified to become the reduction of water.
APPENDIX B

RAMAN PEAK LOCATIONS OF POWDERS AND FILMS

Raman spectroscopy was performed according to Section 4.2. The vibrational modes were observed, and the peak locations were tabulated in Table 11 for powders and in Table 12 for films.

Table 11: Raman spectroscopy results for wet chemical powders

<table>
<thead>
<tr>
<th>C_{60} Raman Mode</th>
<th>Stock C_{60} Peak Location [cm^{-1}]</th>
<th>Original Protocol Peak Location [cm^{-1}]</th>
<th>New Protocol Peak Location [cm^{-1}]</th>
<th>C_{60} Blank Reaction Peak Location [cm^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_g(1)</td>
<td>270.6</td>
<td>269.3</td>
<td>269.6</td>
<td>267.8</td>
</tr>
<tr>
<td>H_g(2)</td>
<td>431.2</td>
<td>431.5</td>
<td>428.4</td>
<td>428.4</td>
</tr>
<tr>
<td>A_g(1)</td>
<td>495.9</td>
<td>492.9</td>
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<td>491.5</td>
</tr>
<tr>
<td>H_g(3)</td>
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<td>707.7</td>
<td>708.0</td>
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</tr>
<tr>
<td>H_g(4)</td>
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<td>773.8</td>
<td>772.4</td>
<td>770.8</td>
</tr>
<tr>
<td>H_g(5)</td>
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<td>1103.0</td>
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<td>1098.5</td>
</tr>
<tr>
<td>H_g(6)</td>
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<td>1241.1</td>
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<td>1244.5</td>
</tr>
<tr>
<td>H_g(7)</td>
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<td>A_g(2)</td>
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<td>H_g(8)</td>
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<tr>
<td>$^{13}C_{60}$ Raman Mode</td>
<td>Sample 1 Peak Location [cm$^{-1}$]</td>
<td>Sample 2 Peak Location [cm$^{-1}$]</td>
<td>Sample 3 Peak Location [cm$^{-1}$]</td>
<td>Sample 4 Peak Location [cm$^{-1}$]</td>
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<td>-------------------------</td>
<td>----------------------------------</td>
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<td>----------------------------------</td>
</tr>
<tr>
<td>$A_g$(1)</td>
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<tr>
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</tr>
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<td>710.9</td>
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<td>-</td>
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</tr>
<tr>
<td>$A_g$(2)</td>
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<tr>
<td>$H_g$(8)</td>
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<td>1564.8</td>
<td>1570.8</td>
<td>1572.3</td>
</tr>
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</table>
APPENDIX C

IR PEAK LOCATIONS OF POWDERS

IR spectroscopy was performed according to Section 4.5. The peaks according to the Opus software are recorded in Table 13.

<table>
<thead>
<tr>
<th>Stock C₆₀ Peak Location [cm⁻¹]</th>
<th>Original Protocol Peak Location [cm⁻¹]</th>
<th>New Protocol Peak Location [cm⁻¹]</th>
<th>C₆₀ Blank Reaction Peak Location [cm⁻¹]</th>
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</thead>
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The heat capacity of the original protocol powder was determined using MDSC. MDSC was performed according to Section 4.7 and the reversible heat capacity results are shown in Figure 33.

Figure 33: Reversible heat capacity results for original protocol powder from MDSC
The thermal diffusivity of the original powder was determined using laser flash analysis. Laser flash analysis was performed according to Section 4.6 and the results are shown in Figure 34. The thermal diffusivities appeared to a slightly decrease as function of temperature between -25 to 50 °C; however, the results from 75 to 300 °C showed no trends above background noise. A possible cause of the noise is due to the pellet’s mechanical state. As the pellet used for laser flash analysis was one of the four pieces from the original pellet, there is a high likelihood that the pellet contained internal fractures. Although previously assumed to be negligible, heating induced thermal expansion could have interfered with the results; thereby appearing as noise in the results. However, since the thermal diffusivity showed relatively small variation, the results were kept and used in thermal conductivity calculations.
Figure 34: Thermal diffusivity results from laser flash analysis for original protocol powder