

YTTERBIUM BASED ALLOYS FOR SPACE-BASED THERMOELECTRIC COOLING
APPLICATIONS

By

Gloria Jeannine Lehr

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Materials Science and Engineering – Doctor of Philosophy

2014

ABSTRACT

YTTERBIUM BASED ALLOYS FOR SPACE-BASED THERMOELECTRIC COOLING APPLICATIONS

By

Gloria Jeannine Lehr

Solid-state thermoelectric devices are of great interest for researchers in many fields due to their potential to increase the efficiency of electrical power generation as well as provide localized heating or cooling in inconvenient environments. Improving the thermoelectric properties of the materials used in these devices is critical to improve their efficiencies and thus feasibility for niche applications. Unfortunately, several of the underlying materials properties are inversely correlated making the thermoelectric figure of merit difficult to improve. In addition, the performance of traditional semiconducting materials is degraded as the operating temperature is decreased. Thus, a unique approach must be taken to achieve larger thermoelectric figures of merit at low temperatures. The research presented here investigates the use of intermediate valence Yb-based compounds for Peltier cooling in the cryogenic regime.

These Yb-based intermediate valence compounds demonstrate large Seebeck coefficients at low temperatures, which is essential to a large figure of merit. The Seebeck coefficient is related to the fluctuating Yb valence, a relationship that is investigated in several compounds and utilized to maximize the thermoelectric figure of merit. Solid solutions are synthesized in order to reduce the lattice thermal conductivity as well as alter the size of the unit cell. Changes in the unit cell volume may contribute to a change in the average Yb valence, and thus be utilized to tune the magnitude and peak temperature of the Seebeck coefficient. By reducing the lattice thermal conductivity and optimizing the Seebeck coefficient, enhancements in the thermoelectric figure of merit can be achieved.

To my family and friends for their unwavering support,
endless encouragement and unconditional love.

ACKNOWLEDGEMENTS

I am extremely grateful for the guidance and support I have received over the years from my advisor and mentor, Dr. Donald Morelli. I would like to thank him for the opportunities he has afforded me to not only conduct this research but also to travel near and far to present and publish my results. I would also like to thank current and former members of the Morelli lab for their hard work, collaboration, and helpful discussions throughout my graduate studies:

Vijayabarathi Ponnambalam, Kevin Zhou, Eric Skoug, Chang Liu, Hui Sun, Steven Boona, Xu Lu, Winston Carr, Spencer Waldrop, and Jared Williams. In addition, many thanks to Travis Thompson for his insightful conversations and unique perspective.

I am also very thankful for my doctoral committee members Drs. Martin Crimp, S.D. Mahanti, and K. Subramanian for their counsel and guidance along the way. Collaborators Dr. Joseph Heremans and Hyungyu Jin (Ohio State University) have been critical to my success as a researcher and are greatly appreciated, as well as Dr. Reza Loloee (MSU-Physics), Karl Dersch (MSU-ECE) and the many other faculty, staff and students at MSU who have assisted me.

I am indebted to Dr. Christopher Fasano (Monmouth College), without whom I would not have attended graduate school. He instilled in me a passion for science and provided me with the strong foundation upon which this work is built.

Finally, I would like to acknowledge the Air Force Office of Scientific Research for funding this project under Multi-University Research Initiative (MURI), “Cryogenic Peltier Cooling,” under Contract Number FA9550-10-1-0533.

TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF FIGURES	vii
Chapter 1 Introduction.....	1
1.1 Thermoelectric Effects	1
1.1.1 Seebeck Effect	1
1.1.2 Peltier Effect.....	3
1.1.3 Thomson Effect	3
1.2 Thermoelectric Devices and Applications	4
1.2.1 Power Generation	6
1.2.2 Thermoelectric Refrigeration	8
1.3 Thermoelectric Performance	10
1.3.1 Contraindicated Properties	11
Seebeck Coefficient	12
Thermal Conductivity	13
1.3.2 Approaches for Enhancing zT	14
Chapter 2 Intermediate Valence.....	19
2.1 Intermediate Valence.....	19
2.2 Theoretical Understanding	20
Chapter 3 Methodology.....	26
3.1 Synthesis.....	26
3.1.1 Arc Melting	26
3.1.2 Homogenization	27
3.1.3 Chemical Etching	27
3.1.4 Ball Milling	28
3.1.5 Densification	29
3.2 Characterization	30
3.2.1 Density.....	30
3.2.2 X-ray Diffraction	31
3.2.3 Scanning Electron Microscopy	31
3.3 Property Measurement	32
3.3.1 Transport Properties	32
3.3.2 Magnetic Properties.....	33
Chapter 4 YbAl₃-Based Solid Solutions.....	35
4.1 Introduction	35
4.2 Pure YbAl ₃	37
4.2.1 Synthesis.....	37
4.2.2 Characterization.....	38
4.2.3 Transport Properties	40
4.3 Yb _{1-x} Sc _x Al ₃	40
4.3.1 Synthesis.....	40

4.3.2 Characterization.....	41
4.3.3 Transport Properties	45
4.4 Yb _{1-x} Er _x Al ₃	49
4.4.1 Synthesis.....	49
4.4.2 Characterization.....	50
4.4.3 Transport Properties	52
4.5 Yb _{1-x} Lu _x Al ₃	56
4.5.1 Synthesis.....	57
4.5.2 Characterization.....	58
4.5.3 Transport Properties	59
4.6 Summary	63
Chapter 5 YbAl₂-Based Solid Solutions.....	66
5.1 Introduction	66
5.2 Yb _{1-x} Sc _x Al ₂	67
5.2.1 Synthesis.....	68
5.2.2 Characterization.....	69
5.2.3 Transport Properties	72
5.2.4 Magnetic Properties.....	76
5.3 Summary	81
Chapter 6 YbCu₂Si₂-Based Solid Solutions	84
6.1 Introduction	84
6.2 YbCu ₂ Si _{2-x} Ge _x	86
6.2.1 Synthesis.....	86
6.2.2 Characterization.....	87
6.2.3 Transport Properties	90
6.2.4 Magnetic Properties.....	93
6.3 Yb _{1-x} La _x Cu ₂ Si ₂	96
6.3.1 Synthesis.....	96
6.3.2 Characterization.....	97
6.3.3 Transport Properties	99
6.3.4 Magnetic Properties.....	103
6.4 Summary	106
Chapter 7 Conclusions.....	108
REFERENCES.....	113
REFERENCES.....	114

LIST OF FIGURES

Figure 1-1: Schematic of thermocouple where A and B are different materials.	2
Figure 1-2: Thermoelectric unit operating in refrigeration mode	4
Figure 1-3: Thermoelectric Device: Composed of many uncouples, these devices can be fabricated in many shapes and sizes.	5
Figure 1-4: Of all of the energy produced in the United States, waste heat accounts for nearly two-thirds. From <i>Lawrence Livermore National Lab and Department of Energy</i> (2013). [13].....	6
Figure 1-5: Power Factor is optimized for highly doped semiconductors. Adapted from Snyder and Toberer <i>Nature</i> (2008). [21].....	12
Figure 1-6: Thermal conductivity of the Si-Ge alloy as a function of Si concentration.....	16
Figure 2-1: A) Ideal delta function, B) Lorentzian function, C) Lorentzian function superimposed on a background DOS ($\sim E^{1/2}$).	22
Figure 3-1: Sample mounting configuration for transport property measurements	33
Figure 4-1: Unit cell diagram of YbAl_3	36
Figure 4-2: The Ytterbium-Aluminum binary phase diagram by Gschneider and Calderwood [79].....	37
Figure 4-3: XRD patterns of each step in the YbAl_3 synthesis process as labeled: A) after the nominal YbAl_3 was arc melted - * indicate peaks from the pure Al phase, B) after sample is etched in NaOH to remove excess Al, C) after YbAl_3 is ball milled, D) after densification using PECS – unlabeled peaks are oxide impurity phase.	39
Figure 4-4: The Sc-Al phase diagram showing the congruent melting of the ScAl_3 phase [84]..	41
Figure 4-5: XRD pattern for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where A) $x = 0.0$, B) $x = 0.25$, C) $x =$ 0.50 , D) $x = 0.75$, E) $x = 1.0$ – unlabeled peaks are from the oxide impurity phase.	43
Figure 4-6: Lattice parameters for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $0 \leq x \leq 1$ at room temperature. Closed symbols come from literature data [79, 81].....	43
Figure 4-7: SEM images of fractured surfaces for A) YbAl_3 and B) ScAl_3	44
Figure 4-8: Electrical resistivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x =$ $0.0, 0.25, 0.5, 0.75$, and 1.0 . Dashed lines are guides to the eye.	45

Figure 4-9: Seebeck coefficient from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.5, 0.75, \text{ and } 1.0$	46
Figure 4-10: Power Factor from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75, \text{ and } 1.0$	47
Figure 4-11: Total thermal conductivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75, \text{ and } 1.0$	48
Figure 4-12: Dimensionless figure of merit from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75, \text{ and } 1.0$	48
Figure 4-13: The Erbium-Aluminum binary phase diagram by Gschneider and Calderwood [85].	50
Figure 4-14: XRD pattern of the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution at room temperature where A) $x = 0$, B) $x = 0.25$, C) $x = 0.50$, D) $x = 0.75$. and E) $x = 1.0$	51
Figure 4-15: SEM images of fractured surfaces for ErAl_3	51
Figure 4-16: Electrical resistivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75, \text{ and } 1.0$	52
Figure 4-17: Seebeck coefficient from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, \text{ and } 0.50$	53
Figure 4-18: Power factor from 80K to 350K for the solid solution $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ where $x = 0.0, 0.25, \text{ and } 0.50$	54
Figure 4-19: Lattice thermal conductivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, \text{ and } 0.50$	54
Figure 4-20: Total thermal conductivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, \text{ and } 0.50$	55
Figure 4-21: The dimensionless figure of merit from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, \text{ and } 0.50$	56
Figure 4-22: The Lutetium-Aluminum binary phase diagram by H. Okamoto [86].	57
Figure 4-23: XRD pattern of the $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ solid solution at room temperature where A) $x = 0.0$, B) $x = 0.25$, C) $x = 0.50$, D) $x = 0.75$, and E) $x = 1.0$	58
Figure 4-24: SEM images of fractured surfaces for LuAl_3	59
Figure 4-25: The electrical resistivity from 80K to (300K) 350K for $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ where $x = 0.0, 0.25, 0.50, 0.75, \text{ and } 1.0$	60

Figure 4-26: The Seebeck coefficient from 80K to (300) 350K for the $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0	60
Figure 4-27: The power factor from 80K to (300K) 350K for the $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0	61
Figure 4-28: The lattice thermal conductivity from 80K to (300K) 350K for $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0	62
Figure 4-29: The total thermal conductivity from 80K to (300K) 350K for the $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0	62
Figure 4-30: The thermoelectric dimensionless figure of merit from 80K to (300K) 350K for $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0	63
Figure 5-1: Unit cell diagram of YbAl_2	66
Figure 5-2: The XRD patterns at room temperature following the each of the steps in synthesizing YbAl_2 . A) after arc melting nominal YbAl where unlabeled peaks indicate a pure Yb phase, and B) pure YbAl_2 phase after 24 hour heat treatment.	69
Figure 5-3: The XRD patterns for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where A) $x = 0.60$, B) $x = 0.70$, C) $x = 0.80$, D) $x = 0.85$, E) $x = 0.90$, F) $x = 0.95$, and G) $x = 1.0$	70
Figure 5-4: The unit cell volume as a function of Sc concentration at room temperature for $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ where $x = 0.0 \leq x \leq 1.0$. Closed circles are data from literature [57].....	70
Figure 5-5: SEM images of fractured surfaces for A) $\text{Yb}_{0.60}\text{Sc}_{0.40}\text{Al}_2$ and B) ScAl_2	71
Figure 5-6: The electrical resistivity from 2K (80K) to 300K (350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0$ [93], $0.60, 0.70, 0.80, 0.85, 0.90, 0.95$, and 1.0	72
Figure 5-7: The Seebeck coefficient from 2K (80K) to 300K (350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0$ [93], $0.60, 0.70, 0.80, 0.85, 0.90, 0.95$, and 1.0	73
Figure 5-8: The power factor from 2K (80K) to 300K (350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0$ [93], $0.60, 0.70, 0.80, 0.85, 0.90, 0.95$, and 1.0	74
Figure 5-9: The total thermal conductivity from 2K (80K) to 300K (350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90$, and 0.95	74
Figure 5-10: The zT from 2K(80K) to 300K(350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90, 0.95$, and 1.0	76
Figure 5-11: The corrected magnetic susceptibility data (points) and the corresponding ICF model fits (lines) from 2K to 300K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90$, and 0.95	78

Figure 5-12: Comparison of the temperatures at which the magnitude of the Seebeck coefficient and the magnetic susceptibility are maximized as a function of Sc concentration.....	78
Figure 5-13: The average Yb valence as a function of temperature obtained from the ICF model for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90$, and 0.95	79
Figure 5-14: The Seebeck coefficient as a function of the average Yb valence for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90$, and 0.95	80
Figure 6-1: Unit cell diagram of YbCu_2Si_2	85
Figure 6-2: XRD patterns for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution.....	87
Figure 6-3: The unit cell volume increases linearly as the Ge concentration is increased in the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution. Solid circles represent literature data [92]......	88
Figure 6-4: SEM images of fractured surfaces for A) YbCu_2Si_2 and B) YbCu_2Ge_2	89
Figure 6-5: The electrical resistivity for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75$ and 2.0	90
Figure 6-6: The Seebeck coefficient for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75$ and 2.0	91
Figure 6-7: The power factor for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75$ and 2.0	91
Figure 6-8: The thermal conductivity for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75$ and 2.0	92
Figure 6-9: The zT for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75$ and 2.0	93
Figure 6-10: The corrected magnetic susceptibility for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $0 \leq x \leq 2$. Solid lines are fits to the ICF model.	94
Figure 6-11: The average Yb valence as a function of temperature for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $0 \leq x \leq 2$	94
Figure 6-12: The Seebeck coefficient vs. average Yb valence for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $0 \leq x \leq 2$	95
Figure 6-13: Comparison of the temperatures at which the magnitude of the Seebeck coefficient and the magnetic susceptibility are maximized as a function of Ge concentration.	96
Figure 6-14: XRD patterns collected at room temperature for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where A) $x = 0$, B) $x = 0.20$, C) $x = 0.40$, D) $x = 0.60$, E) $x = 0.80$, and F) $x = 1.0$	97

Figure 6-15: The unit cell volume increases linearly as the La concentration is increased in the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution. Solid circles represent literature data.....	98
Figure 6-16: SEM images of fractured surfaces for LaCu_2Si_2	98
Figure 6-17: The electrical resistivity for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95,$ and 1.0	99
Figure 6-18: The Seebeck coefficient for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95,$ and 1.0	100
Figure 6-19: The power factor for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95,$ and 1.0	101
Figure 6-20: The thermal conductivity for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95,$ and 1.0	102
Figure 6-21: The zT for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95,$ and 1.0	102
Figure 6-22: The corrected magnetic susceptibility for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95,$ and 1.0	104
Figure 6-23: The average Yb valence as calculated from the ICF model from 2K to 300K for $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ where $x=0, 0.05, 0.10, 0.15,$ and 0.20	104
Figure 6-24: The Seebeck coefficient as a function of the average Yb valence for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15,$ and 0.20	105
Figure 7-1: The average Yb valence vs. the unit cell volume for three solid solutions shows that the Yb valence state is dependent on the available space in the unit cell.	110
Figure 7-2: The Seebeck coefficient vs. average Yb valence for each of the Yb-based intermediate valence compounds investigated in this work.	111

Chapter 1 Introduction

Energy efficiency has become a widespread household concern, whether it is lighting, appliances, or vehicle fuel efficiency. The US Department of Energy and other government agencies spend millions of dollars on research to improve the efficiency of different energy processes. One way to improve energy efficiency is to recapture the heat that is expelled as a wasted byproduct from a generator or other device and convert it into useable electricity. Conversion of this wasted heat to electricity can be achieved by incorporating solid-state thermoelectric devices into the system. These thermoelectric devices can also be used as localized heaters/refrigerators when a current is passed through the device creating a temperature gradient. Thermoelectric devices are important for niche applications that require precise temperature control, such as medicinal storage units, laboratory equipment, and even high-end computing systems.

1.1 Thermoelectric Effects

The thermoelectric effects that are implemented in solid-state thermoelectric devices today were discovered long ago, but were not completely understood for quite some time. Three fundamental effects that were discovered in the 19th century are known as the Seebeck Effect, Peltier Effect, and the Thomson Effect. Fully understanding how these effects work is critical to optimizing thermoelectric materials and thus increasing the efficiency of thermoelectric devices.

1.1.1 Seebeck Effect

The Seebeck effect was first discovered in 1821 when Thomas Johann Seebeck found that a circuit made of two different metals deflected the needle of a magnet when the junctions were

held at different temperatures. Seebeck believed that the magnetic field was created directly by the temperature gradient and that this effect could explain Earth's magnetic poles [1]. It was later discovered that this magnetic field was actually created by an electric current flowing through the circuit. Despite Seebeck's incorrect interpretation of the effect, he is still credited with the discovery that a temperature gradient at the junctions of two dissimilar materials causes an electrical current to flow [2–6].

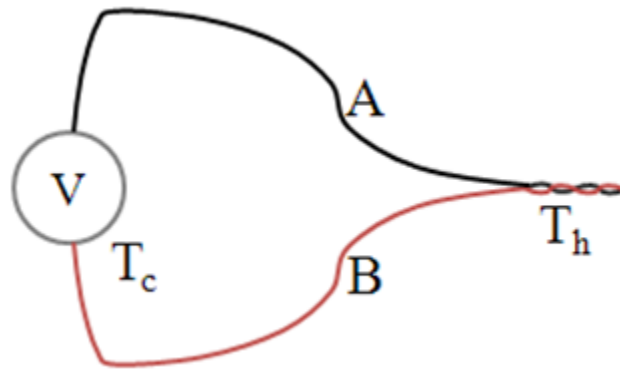


Figure 1-1: Schematic of thermocouple where A and B are different materials.

The Seebeck effect is the basis for the thermocouple, which consist of two wires of dissimilar materials joined together. In order for a thermocouple to work, the two wires create a circuit, across which a voltage is measured. Figure 1-1 shows a schematic of a thermocouple, where the temperature difference ($T_h - T_c$) is determined by measuring the voltage across two different materials (A and B). This measured voltage and a proportionality constant, known as the Seebeck coefficient, can be used to calculate the temperatures of the two junctions using the following formula:

$$V = S(T_h - T_c) \quad \text{Equation 1}$$

where V is the voltage measured across the circuit of the two different materials, S is the Seebeck coefficient, T_h is the hot side temperature, and T_c is the cold side temperature.

1.1.2 Peltier Effect

In 1834 Jean Charles Athanase Peltier discovered that a current passed through a circuit of two dissimilar materials caused one junction to be heated and the other cooled [3–5]. This heating/cooling effect was switched when the direction of the current was reversed. The heat generated at a junction per unit time, Q , can be described as:

$$Q = (\Pi_A - \Pi_B)I \quad \textbf{Equation 2}$$

where Π is the Peltier coefficient for materials A or B and I is the electric current from A to B [3,7]. This Peltier refrigeration (and heating) was very clearly demonstrated in 1838 by Heinrich Lenz when he placed a drop of water at the junction of two wires, made of bismuth and antimony, and then passed a current through the circuit. Passing the current through the junction in one direction caused the water to freeze while reversing the direction of the current caused the ice to melt [3–5].

1.1.3 Thomson Effect

Sir William Thomson, also known as Lord Kelvin, also contributed to the field of thermoelectrics by improving the interpretation and understanding of the Seebeck and Peltier effects. Thomson noted that the Peltier effect is the reverse of the Seebeck effect, and that these coefficients are thermodynamically related by the Kelvin relation as:

$$\Pi = ST \quad \textbf{Equation 3}$$

where T is the temperature in Kelvin [3]. This relationship is used for simplicity, and today, only the Seebeck coefficient is used in thermoelectric studies and reports. Thomson also observed that heating or cooling occurs in different segments of a single material as a current is passed through the material as long as a temperature gradient is maintained across the material. This is known as the Thomson effect and can be thought of as a continuous version of the Peltier effect.

1.2 Thermoelectric Devices and Applications

Based on these fundamental effects, a thermoelectric device can operate either as a thermoelectric generator (TEG) or as a thermoelectric cooler (TEC). These devices are all solid-state, meaning that there are no moving parts in the system. Currently, thermoelectric devices are not widespread commercially due to their low efficiencies, which are limited by the materials used in the device. There is substantial interest in thermoelectrics research as there is a long list of potential applications for both TEGs and TECs fueling the research on material improvements.

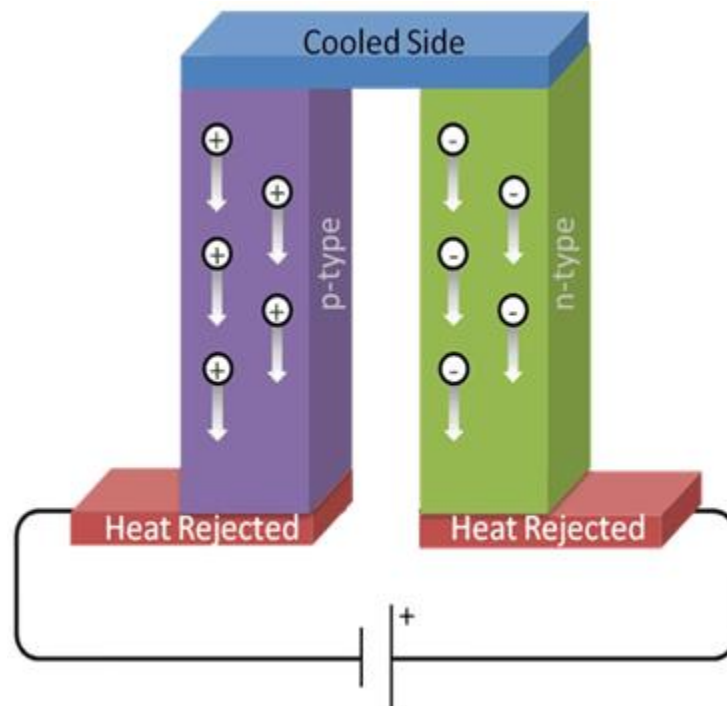


Figure 1-2: Thermoelectric unit operating in refrigeration mode

Thermoelectric generators and thermoelectric cooling devices are both designed in the same manner. In order to operate, these devices require two dissimilar materials arranged as a circuit. If a temperature gradient is applied across this circuit, a current is established as

discussed in the explanation of the Seebeck effect (Section 1.1.1). If a current is applied to the circuit, one of the junctions is cooled and the other junction is heated as discussed in the Section 1.1.2 on the Peltier effect. These two dissimilar materials are known as n-type and p-type. N-type materials have electrons as the dominant charge carrier, and a negative Seebeck coefficient. Conversely, p-type materials use holes as the dominant charge carrier and have a positive Seebeck coefficient. These n- and p-type materials make up the two parallelepiped legs, shown in Figure 1-2, known as a unicouple. Any number of these unicouples may be arranged together, electrically in series and thermally in parallel to create a thermoelectric device, generally in an arrangement similarly to that shown in Figure 1-3 [8]. Arranging these unicouples thermally in parallel helps to maintain the temperature gradient across each element of the device, while placing them electrically in series allows for an increased voltage output.

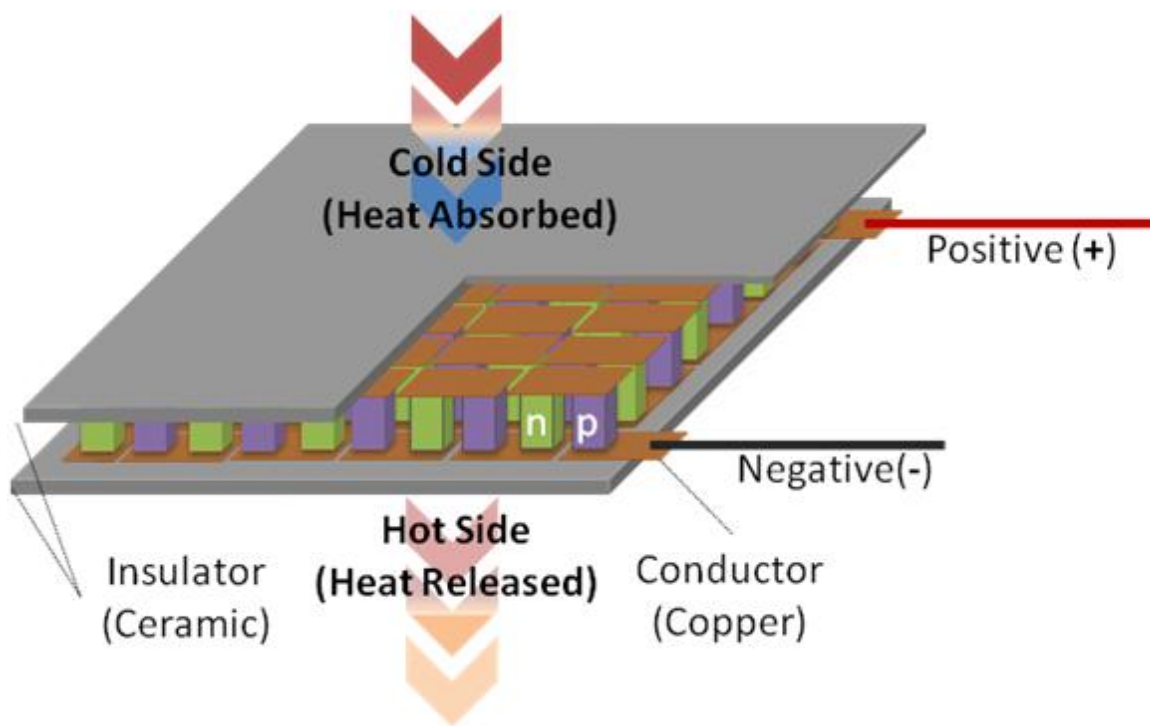


Figure 1-3: Thermoelectric Device: Composed of many unicouples, these devices can be fabricated in many shapes and sizes.

1.2.1 Power Generation

Thermoelectric devices operating in power generation mode convert a temperature gradient into an electrical current. This phenomenon occurs because of the Seebeck effect. TEGs have been widely used over the past 50 years in space exploration missions such as Voyager 1 and 2, Galileo, the Mars Curiosity Rover, and many other satellites/spacecraft [9,10]. In these applications, a radioactive material provides the heat source, which TEGs convert into a usable electrical current to power the sensors and other electronics aboard the spacecraft [9]. TEGs are optimal for this type of application because they are reliable; having an infinite theoretical lifetime with no moving parts and the power they provide does not fluctuate as long as the temperature gradient is maintained. These devices are also known to perform well in harsh environments, such as the vacuum of deep space [11,12].

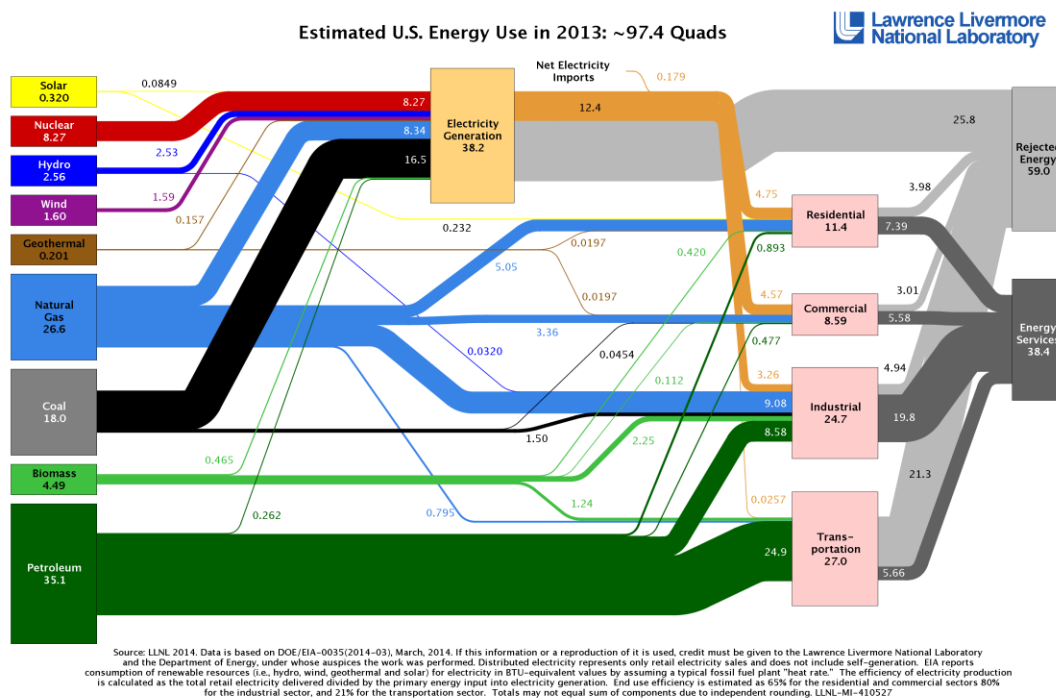


Figure 1-4: Of all of the energy produced in the United States, waste heat accounts for nearly two-thirds. From *Lawrence Livermore National Lab and Department of Energy* (2013). [13]

Apart from space applications, TEGs have also gained attention terrestrially for their environmentally friendly operation, which can improve the efficiency of any energy related process. Of all of the energy produced in the United States, whether it be from renewable resources or fossil fuels, only 40% is actually utilized, while the remaining 60% is wasted, typically in the form of heat, as seen in Figure 1-4 [13]. This statistic demonstrates the impact that TEGs could have in reducing the cost of electricity or increasing the efficiency of countless processes if integrated on a large scale. Current TEGs are capable of converting between 5% and 10% of wasted heat into electricity [3,11,12,14,15]. While this number sounds small, it is much more significant when we consider that the heat needed for these TEGs to operate is essentially free, as it is already being produced and expelled as waste.

Many industries could benefit greatly if thermoelectric efficiencies were improved enough to make them commercially viable solutions. One such application that is widely researched is in the automotive industry [12], where TEGs could convert waste vehicle exhaust heat into electricity. The average automobile on the road releases roughly 2/3 of its energy as heat through the exhaust and radiator; only the remaining 1/3 is actually available to power the car and drive auxiliary components [16]. The electricity produced by the TEGs could be used to power accessories, such as the radio, power windows and locks, navigational systems, etc., that currently draw off of the engine and reduce the vehicle's fuel efficiency. There are many challenges to successfully integrating TEGs into an automotive system. For example, the temperature of the exhaust gas dramatically fluctuates based on the driving cycle, while each thermoelectric module has a small optimal temperature range. Therefore, when the exhaust gas is not at the ideal temperature, the TEG does not produce much or any electricity, rendering the entire device an unnecessary added weight. In addition, the thermoelectric materials must be able

to handle thermal cycling without degradation of their thermoelectric or mechanical properties. The mechanical strength of the thermoelectric materials involved is another issue that must be addressed. These TEG devices would be attached under the car (similarly to a muffler); therefore, they must endure many bumps and vibrations. Many of today's best thermoelectric materials are rather brittle and would not likely withstand this type of environment. Despite all of the engineering challenges, the fuel efficiency returns could be great enough that many automotive companies are investing significant time and money into overcoming these hurdles.

Enhancing the power conversion efficiency of thermoelectric materials would also make TEGs an economic option for recovering waste heat from industrial and manufacturing power plants [12]. There is a significant amount of waste heat that is expelled from these plants in gas or liquid form because it is no longer at an adequate temperature for conventional power generation systems. However, TEGs optimized for this temperature range could be utilized to regain some of this lost energy and increase the amount of power produced with zero excess fuel. As the materials in TEGs become cost effective enough to manufacture and/or efficient enough to justify their cost, integration of these thermoelectric power generators is inevitable. In the last year, the first commercially available thermoelectric power generator was produced and announced for industrial applications by Alphabet Energy. This waste heat generator is capable of generating electricity at approximately 2.5% efficiency [17]. Further research is still needed to improve the thermoelectric properties of the materials and enhance the electrical output of these generators.

1.2.2 Thermoelectric Refrigeration

Thermoelectric cooling/refrigeration, also known as Peltier cooling/refrigeration, operates similarly to the power generators, only in reverse. These thermoelectric coolers (TECs) function

based on the Peltier effect, which was explained in Section 1.1.2. A current is supplied to the device and one side is cooled while the other side is heated. Reversing the direction of the current switches which side of the device heats and which side cools. TECs are currently not widespread; however, in niche applications where precise temperature control is the priority, rather than energy efficiency, these solid-state devices are often implemented.

A few examples where TECs are used are: in laboratory equipment where specimens must be held at a very specific temperature, in many wine coolers, for the heating and cooling of upscale automotive seats, and as coolers for expensive computer systems [12,18]. There are many other applications where TECs could be used if their efficiencies were better. One particular application, at which this study is directed, is for cooling infrared sensors located on satellites orbiting the earth [12,19].

While space is fundamentally thought of as “cold” it is also a vacuum, and therefore any heat that is produced does not diffuse away from the source, causing electronics in space to become quite hot. This problem is addressed via cooling systems that are implemented in all satellites. Infrared sensors, however, pose a slightly more difficult problem, because in order to operate properly they must be cooled to cryogenic temperatures. Previously, liquid helium or nitrogen was used to cool such devices, requiring large pressurized dewars, which, regardless of capacity, have a relatively short lifetime. The current state-of-the-art technology for cooling these infrared sensors utilizes mechanical cooling systems known as cryocoolers [20]. These cryocoolers operate on fundamental thermal cycles, such as Joule-Thomson, that require compression and expansion of gasses for cooling. While these mechanical cryocoolers are successful at the given task, there are many issues with the basic idea of using mechanical devices in space. The nature of mechanical systems is that over time the moving parts wear out

and break down, becoming a major concern when the primary function of the device is to operate in orbit. The moving parts in this device also create vibrations that are not desirable for sensitive components, such as infrared sensors. It is also very difficult to scale down these devices to smaller sizes without greatly reducing the efficiency. Finally, mechanical cryocoolers are very expensive to produce and tune, require costly electronics, and they also add a significant cost to the launch, as they are quite heavy [20]. Despite this list of negative attributes, to date mechanical cryocoolers are the best solutions currently available for cooling infrared sensors.

This work is aimed at improving the thermoelectric properties of thermoelectric materials at low temperatures, in hopes of replacing these mechanical cryocoolers with cryogenic TECs. TECs can solve many of the problems that plague mechanical cryocoolers because of their all solid state nature [5,6,21]. There are no moving parts to wear out and break down, and therefore, no unwanted vibrations are added to the infrared sensor system. These TECs would weigh less and likely cost much less to produce, making them a very attractive option. Finally, unlike mechanical cryocoolers, the efficiency of a TEC scales with the size of the device, and therefore devices can be custom made for each infrared sensor detector as necessary. However, the thermoelectric properties of typical thermoelectric materials are dramatically reduced below room temperature and have essentially zero efficiency in the cryogenic range. Therefore, a new approach to thermoelectrics with unique materials is reported here in the study of ytterbium-based thermoelectric alloys.

1.3 Thermoelectric Performance

In order to understand and compare the performance of thermoelectric materials, a single value, known as the thermoelectric dimensionless figure of merit, zT , is used. This value incorporates the electrical conductivity (σ), thermal conductivity (κ), the Seebeck coefficient (S), and

operating temperature (T) as:

$$zT = \frac{S^2 \sigma}{\kappa} T \quad \text{Equation 4}$$

This value is useful because all thermoelectric materials, regardless of optimal operating temperature, can be directly compared. The zT of each material can also be used to determine the theoretical conversion efficiency (η) of a TEG or coefficient of performance (ϕ) of a TEC [22].

$$\eta = \frac{\Delta T}{T_H} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}} \quad \text{Equation 5}$$

$$\phi = \frac{T_C}{\Delta T} \frac{\sqrt{1+ZT}-\frac{T_H}{T_C}}{\sqrt{1+ZT}+1} \quad \text{Equation 6}$$

Although the zT is a fairly simple equation, it is made up of properties that are intertwined with one another, making it difficult to tune them independently and optimize the zT value.

1.3.1 Contraindicated Properties

Electrical Conductivity

Several of the properties in the zT equation are “contraindicated,” in other words, optimizing one property ultimately decreases the value of another property. As can be seen in Figure 1-5 [21], as the number of charge carriers (either electrons or holes) is increased, the electrical conductivity increases [21]. This is because there are a larger number of charge carriers (n), and the electrical conductivity goes as:

$$\sigma = ne\mu \quad \text{Equation 7}$$

where e is the charge of the carrier and μ is the carrier mobility.

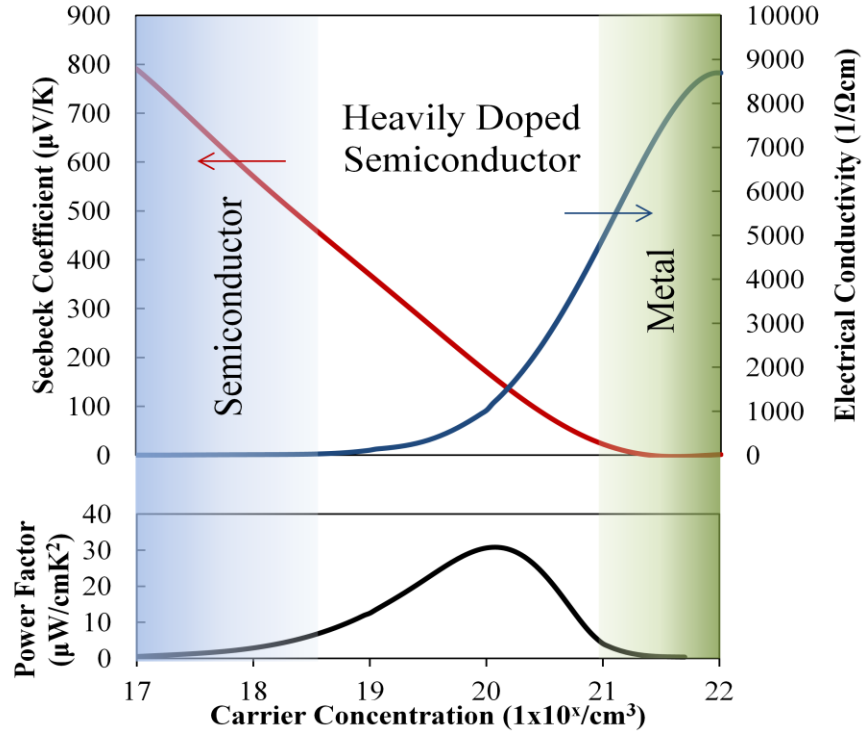


Figure 1-5: Power Factor is optimized for highly doped semiconductors. Adapted from Snyder and Toberer *Nature* (2008). [21]

Seebeck Coefficient

Figure 1-5 also shows that as the number of charge carriers increases the Seebeck coefficient decreases. For metals or degenerate semiconductors the Seebeck coefficient can be expressed as :

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad \text{Equation 8}$$

where k_B is the Boltzmann constant, h is Planck's constant, and m^* is the effective mass of the charge carrier [20]. This expression clearly shows that increasing n has a detrimental effect on the Seebeck coefficient. There is also a relationship between the effective mass and the carrier concentration, in which if one is increased the other is decreased. This affects both the Seebeck coefficient and the electrical conductivity, as a large effective mass is good for the Seebeck coefficient, but bad for electrical conductivity [21]. Both the Seebeck coefficient and the

electrical conductivity fall in the numerator of the zT value, and $S^2\sigma$ is referred to as the power factor. Because of these contraindicated properties, there is an optimal range for the number of carriers in which the power factor is maximized in a thermoelectric material, generally between 10^{19} and 10^{21} carriers/cm³, which is typically found in heavily doped semiconductors or semimetals.

The Seebeck coefficient is also proportional to the derivative of the electron density of states at the Fermi level as described by the Mott relation [4]:

$$S = \left(\frac{\pi^2}{3}\right) \left(\frac{k_B^2 T}{e}\right) \frac{1}{\sigma} \left(\frac{d\sigma}{dE}\right)_{E=E_F} \quad \text{Equation 9}$$

Here it is apparent that as the electrical conductivity is increased the Seebeck coefficient is decreased. However, the rate of change of the DOS is also directly related to the Seebeck coefficient. This description is useful, because it gives an idea of the type of band structure that is desired for a good thermoelectric material. Ideally, the Fermi level would pass through the top of a flat conduction band (or bottom of the valence band for p-type). If looking at a plot of the density of states, the Fermi level should be near the peak, but slightly offset in order to pass through the steepest part of the density of states peak, as will be further discussed in Chapter 2. Mahan and Sofo [23] describe the best DOS as a Dirac delta function, however, this is not achievable in real materials.

Thermal Conductivity

Not only are there contraindicated properties within the power factor, but the electrical conductivity and thermal conductivity are also entwined. An ideal thermoelectric material would have a large electrical conductivity with a small thermal conductivity. This is an unrealistic goal because the same charge carriers that are needed to create a large electrical conductivity also contribute to the thermal conductivity. The thermal conductivity can be defined as:

$$\kappa = \kappa_e + \kappa_l \quad \text{Equation 10}$$

where κ_e is the electronic contribution to the thermal conductivity and κ_l is the lattice contribution. The electronic contribution can be calculated from the Wiedemann-Franz law:

$$\kappa_e = L\sigma T \quad \text{Equation 11}$$

where L is the Lorenz number, taken as $2.4 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ for metallic or nearly metallic materials. This relationship demonstrates that increasing σ also increases κ_e thus increasing the total value of κ , which is in the denominator of the zT equation. Therefore arbitrarily increasing σ is generally counterproductive to the overall thermoelectric efficiency of a material.

1.3.2 Approaches for Enhancing zT

The complicated relationships between the thermoelectric properties limit the possible approaches to enhance the figure of merit, making such a task quite difficult. However, several methods have proven successful for optimizing the thermoelectric efficiency of materials. In order to optimize the power factor, the ideal number of carriers for a compound must be found. It is generally faster and more reliable to obtain results experimentally than by theoretical calculations. Changing the carrier concentration or carrier mobility is the only way to alter the electrical conductivity, and thus tuning these properties is the best means available for optimizing the power factor. Secondly, reducing the thermal conductivity of a compound is a very important task for enhancing the zT of a thermoelectric material. However, because of the correlation between the electronic component of the thermal conductivity and the electrical conductivity, the primary focus must be on reducing the lattice component of the thermal conductivity. Below are several approaches for reducing lattice thermal conductivity, which may be implemented independently or in combination to achieve the best results.

Creating solid solutions or alloys is achieved by substituting elements of different sizes and masses for one or more of the original elements in the compound. Typically, solid solutions are made with atoms that have the same number of conduction electrons as the host atom (isoelectronic substitution), to prevent changes to the electronic properties. However, the band structure may be still be altered resulting in systematic changes in the carrier concentration and mobility. Thus, solid solutions can result in changes to the electronic properties. These changes can have either positive or negative effects on the power factor. The substitutional atoms in a solid solution are point defects, which scatter phonons, thus disrupting the flow of the lattice thermal conductivity [24-26]. The larger the mass difference, the more effective the scattering is:

$$r \sim c(1 - c) \left(\frac{\Delta m}{\bar{m}} \right)^2 \quad \text{Equation 12}$$

where r is the scattering rate, c is the impurity concentration, Δm is the mass difference, and $\bar{m}$ is average mass of the atoms in the crystal [26]. Thermodynamic calculations can be used to determine the solubility of a substitutional atom in a compound. Experimentally, candidate substitutional atoms can be found by looking for compounds with the same crystal structure and similar lattice parameter. Although this is not a guarantee, it is common that these two different, but isostructural compounds, will form a full solid solution. A classic example is that of Si-Ge alloys, which form a complete solid solution and reduce the lattice thermal conductivity via point defect scattering and thus increases the figure of merit. Figure 1-6 demonstrates this reduction in the thermal conductivity as Si and Ge are alloyed. A minimum in the thermal conductivity is observed near $x=0.5$ where the number of point defects is maximized [27].

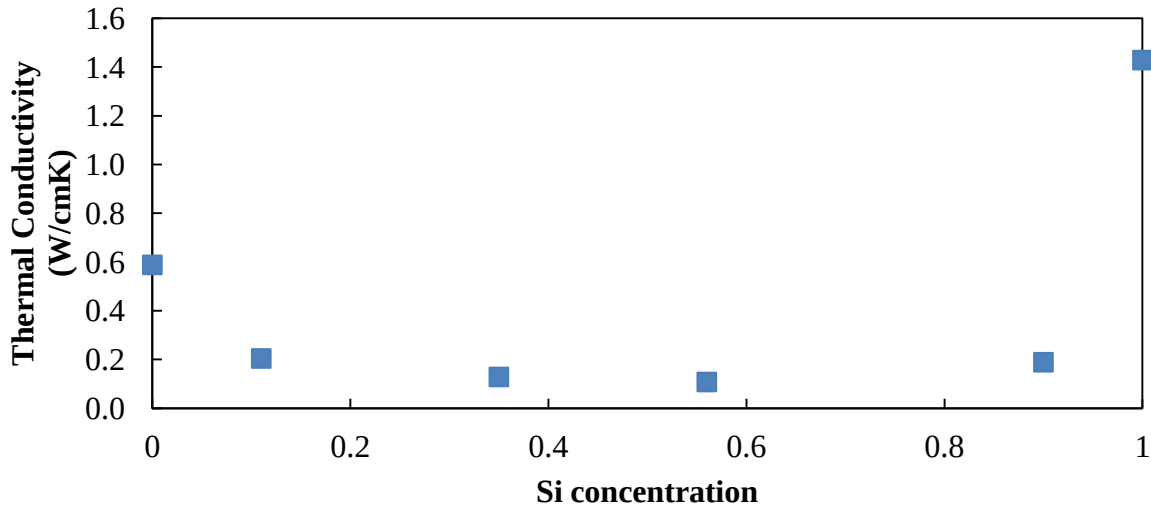


Figure 1-6: Thermal conductivity of the Si-Ge alloy as a function of Si concentration.

Doping is a similar method to solid solutions in that one of the host atoms is replaced; however, in this case, it is replaced with an element with one more or one less electron. The dopant concentration can be tailored to alter the number of charge carriers in order to achieve a carrier concentration in the optimal range. Optimizing this carrier concentration alters the Seebeck coefficient and electrical conductivity to maximize the power factor. Doping can also create disruptions in the phonon propagation, similarly to solid solutions. Dopant atoms are usually not significantly different from the host atom in size or mass, only in the number of electrons, and are typically used in low concentrations. Therefore the phonon scattering effect is not as strong as in solid-solution alloying, but there is still a measurable decrease in the lattice contribution of the thermal conductivity for many doped samples.

Finally, another approach to enhancing the zT is through reduction of the lattice component of the thermal conductivity by reducing the grain size. Particle sizes can be reduced by powder processing [28] samples and using rapid sintering techniques that prevent grain growth [29,30]. High-energy ball mills are often used to create powders with particles in the

nanometer range. These powders must then be densified without significant grain growth. Hot pressing and pulsed electric current sintering are two common ways to densify powders. The time, temperature, and pressure of these processes can be customized for each alloy to achieve high densities with minimal grain growth. This processing can reduce the lattice thermal conductivity as the grain boundaries cause disruption of phonon propagation. Smaller grain sizes means less time between scattering events and thus a higher frequency of disruptions and reduced lattice thermal conductivity [31].

While these methods for increasing power factor and reducing the lattice thermal conductivity have proven to be successful approaches for traditional semiconducting thermoelectric materials, further difficulties exist at lower temperatures. As previously discussed, the focus of this project is to create thermoelectric materials that operate successfully at temperatures in the cryogenic range. Generally speaking as temperature decreases in semiconductors, the number of available carriers is reduced because there is less energy to promote carriers across the band gap. This results in a reduction to the electrical conductivity [29]. The Seebeck coefficient also decreases, approaching zero at zero Kelvin. These changes in the electronic properties with decreasing temperature generally result in extremely low power factors. The reduced electrical conductivity also results in a decreased electronic component of the thermal conductivity; however, reduced temperature also means a decrease in the phonon-phonon scattering in the lattice [32]. Therefore, the total thermal conductivity may actually be enhanced at low temperatures before approaching zero at zero Kelvin, further reducing the zT value.

Due to these fundamental issues with traditional semiconductors, a new approach must be taken in order to discover and develop materials that are optimized for low temperature

performance. Metals are generally ignored in the search for good thermoelectric materials because of their low Seebeck coefficient and large thermal conductivity; however, a particular group of compounds, known as intermediate valence materials, may offer some unique properties that can overcome the issue of small Seebeck coefficient at low temperatures despite their otherwise metallic character [5,23].

Chapter 2 Intermediate Valence Effects

Theoretical and experimental work over the past 60 years has shown that optimizing the thermoelectric effects and achieving large zT in materials at low temperatures is even more challenging than in high temperature materials [12,15,33]. At low temperatures, not only are the Seebeck coefficient and electrical conductivity reduced, but also the temperature itself factors in to reduce the zT value. It has become apparent that traditional doped semiconductors are not necessarily the best materials for low temperature applications. One promising alternative is to use intermediate valence alloys. These materials typically have metallic resistivities, but occasionally also show unusually large peaks in the Seebeck coefficient at low temperatures [23,33–36]. This high electrical conductivity, in addition to the large Seebeck coefficient, result in some of the largest power factors ever reported at room temperature and below [23]. Unfortunately, many of these intermediate valence systems have relatively simple unit cells, and therefore also have very large lattice and total thermal conductivities, reducing the overall zT value.

2.1 Intermediate Valence

Intermediate valence compounds contain one atom in the host matrix that has a fluctuating valence, meaning that one electron state can have either n or $n+1$ electrons at any given moment. Intermediate valence compounds are not to be confused with mixed valence compounds. Mixed valence compounds have a single element that can be in one of two different valence states (two different numbers of valence electrons) according to which lattice site it occupies [37–39]. In an intermediate valence compound, each atom of consequence (Yb in this case) fluctuates in time between two different valence states, regardless of lattice site [39–42]. It is common to refer to a

non-integer value as the valence state of this element, which is actually the average valence. For instance if an atom fluctuates between the 2+ and 3+ valence state, it may have an average valence value of 2.5 if the fluctuating electron is found to exist, on average, in the localized electron-energy state exactly the same amount it is found in the conduction band. However, if the atom favors a divalent state, it may be closer to an average valence state of 2.2 as the electron is more frequently found in the localized state than in the conduction band, and so on. Any non-integer value between 2 and 3 may be assigned to this atom in an intermediate valence compound.

The valence state of an atom can to some extent be determined by the volume available in the lattice for the atom to occupy. This volume can be altered via external or internal pressures. External pressures of several GPa are applied in order to reduce the size of the unit cell and can often force atoms into a valence state with fewer electrons [43-46], which has a smaller atomic radius (more of the electrons move to the conduction band). Chemical pressures can also be used to change the size of the unit cell [39,46–53]. This method allows for expansion or contraction of the lattice by substitution of atoms of larger or smaller atomic radius relative to the host. The ability to stretch the unit cell allows researchers to not only examine the effects of smaller unit cells, but also of larger unit cells on the valence fluctuations.

2.2 Theoretical Understanding

Intermediate valence effects are most commonly found in compounds containing rare-earth elements, and more specifically Ce and Yb-based compounds [5,23,33,34,39,54–59]. These two elements can be thought of as opposites because when Ce fluctuates between two valence states (4+ and 3+) it has an f-shell that is completely empty or contains just one electron, while Yb (2+ and 3+) fluctuates between a completely full f-shell or one containing a single hole. The

dominant carrier in Ce-based compounds is the hole, while in Yb-based compounds, electrons are the dominant charge carrier. Thus, one electron in the f-shell of a Ce-based compound (3+ valence state) is effectively the opposite of one hole in the f-shell of a Yb-based compound (3+ valence state). The simple inverse relationship between Ce- and Yb-based compounds has resulted in many theoretical models and explanations that are applicable to both types of systems.

Previous researchers have done a significant amount of work on understanding the effect that these intermediate valence fluctuations have on different Ce- and Yb-based systems. One of the most commonly observed effects of intermediate valence systems is a minima in the electrical resistivity and peaks in the magnetic susceptibility which are reminiscent of Kondo-like systems. In addition to these interesting features in the electrical resistivity and magnetic susceptibility, intermediate valence compounds are known for large peaks in their Seebeck coefficient in the low temperature regime [33,34,39,58–60]. These peaks are generally attributed to a large peak in the electron density of states (DOS) near the Fermi level. While the Dirac delta function is the ideal electronic transport distribution, it is not a distribution found in real materials. One of the closest approximations found in nature to this delta function is in rare-earth containing compounds which have f-electron levels [23].

Figure 2-1 demonstrates a Dirac delta function, a lorentzian distribution, as well as a more realistic distribution of a lorentzian function superimposed on, or “hybridized” with, a background signal. The f-electron levels are bound tightly about the nucleus, giving rise to the narrow lorentzian like peak in the DOS (Figure 2-1B). The background contribution shown in

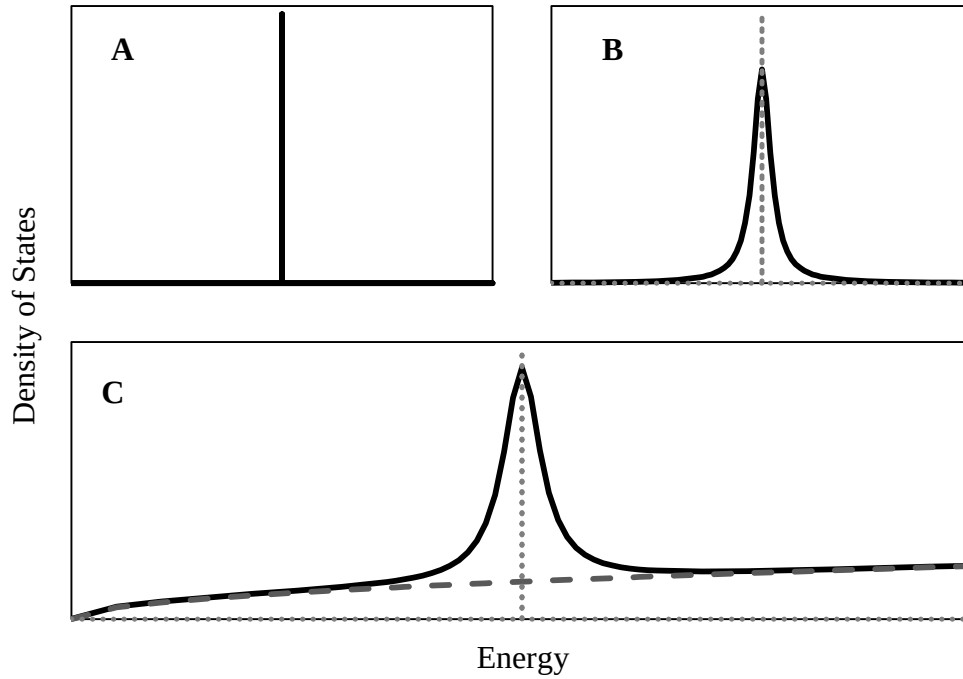


Figure 2-1: A) Ideal delta function, B) Lorentzian function, C) Lorentzian function superimposed on a background DOS ($\sim E^{1/2}$).

Figure 2-1C is 10% of the f-level peak and is approximately proportional to the more classical $E^{1/2}$ distribution that represents the DOS signal from the other orbitals in the system. This background signal can be detrimental to the maximum possible Seebeck coefficient and thus reduce the maximum zT [23,35]. Calculations by Mahan and Sofo show that background DOS contributions of greater than 1% of the f-shell peak are quite detrimental to the maximum zT [23]. In fact, a background contribution of only 10% can reduce the maximum possible figure of merit to only 25% of its original value [23]. Ideally, the sharp singularity in the DOS is very near the Fermi energy, which maximizes the thermoelectric figure of merit. A simple examination of Equation 9, describing the Seebeck coefficient using the Mott relation, shows that the value of the Seebeck coefficient is dependent on the derivative with respect to energy of the density of

states at the Fermi level. Therefore, if the Fermi energy intersects the singular Lorentzian peak at its steepest point, then the Seebeck coefficient will be maximized.

The magnitude of the Seebeck coefficient is greatly dependent on the electronic transport distribution as discussed above; however, the concentration of f-ions can alter the Seebeck coefficient as well [35]. By altering the number of magnetic moments (or f-ions), it is possible to achieve large values of Seebeck coefficient while providing a means to tailor the temperature at which the Seebeck coefficient peaks. Diluting the system via isoelectronic substitution typically weakens the hybridization strength, thus causing a shift in the peak towards lower temperature without significantly reducing the Seebeck coefficient (particularly when compared to compounds without intermediate valence behavior) [33,35]. Both concentrated and dilute quantities of Yb atoms result in interesting features in the magnetic and thermoelectric properties, due to the small spatial reach of the 4f wave functions, which are on the order of one-tenth the interatomic spacing [35]. This means that neighboring Yb atoms have little direct interaction, and therefore even dilute systems demonstrate strong intermediate valence effects. Due to the strong f-shell interactions with the conduction electrons in even dilute compositions, it is possible to study and understand these intermediate valence effects across a wide spectrum of concentrations as well as to maximize the other thermoelectric properties (which may benefit from dilute Yb concentrations) without dramatically affecting the Seebeck coefficient.

Isoelectronic substitutions cannot only shift the temperature dependence of the Seebeck coefficient, but substitutions can also create internal chemical pressure, which can have dramatic effects on the temperature dependence and ultimately the magnitude of the Seebeck coefficient. Both internal (chemical) and external pressures can force the Yb ion toward a more stable trivalent $4f^{13}$ configuration [34], while chemical expansion has the opposite effect, resulting in an

intermediate valence or nearly divalent state for the Yb-ion [57]. The Seebeck coefficient reflects the magnetic stability of the Yb-ions and can be theoretically described as one of four types of temperature dependent shapes, as defined by Zlatic and Monnier [34]. These different types refer to the temperature dependencies of the Seebeck coefficient as having (a) a positive maximum at low temperatures and a negative minimum at high temperatures, which are nearly the same in magnitude, (b) two negative minima with a small positive maximum separating them, (c) a small negative minimum at low temperatures as well as a large negative minimum at high temperatures, and (d) a single negative minimum at high temperatures [34]. Here, high temperature is defined to be near 100K while low temperatures are <30K. By categorizing the shape of the Seebeck coefficient it is possible to understand the magnetic regime of the Yb-ion as magnetic with a stable $4f^{13}$ configuration (type-a), non-magnetic with an unstable intermediate valence configuration (type-d), or somewhere in between (types-b&c). By applying pressure to the system, the compound can be transformed from a type-d shape to a type-c or b shape, and eventually all of the way to a type-a shape as the magnetic moments are stabilized and no longer in the intermediate valence regime [34]. The changes induced by internal pressure/expansion can be optimized in many Yb-based compounds to achieve large peaks in the Seebeck coefficient over a broad temperature range by achieving a shape between type-c and type-d. This shape would ideally have a shoulder on the low temperatures side of a large negative minimum, resulting in the largest overall magnitude of the Seebeck coefficient (near 100K) which is maintained over a relatively broad temperature range. The concentration of substitutional atoms required to achieve this type of optimization is different for each composition and may be determined experimentally, but the theoretical concepts for this approach can be understood by the single-impurity Anderson model [34].

While there is much interesting physics to be explored and understood in these models, the goal here is two-fold: 1) synthesize new materials on a large enough scale to have mechanically robust samples for thermoelectric measurements using common processing techniques and 2) control the magnitude and temperature dependence of the thermoelectric properties of these materials using chemical substitution according to the above discussion. This research will implement these concepts in real Yb-based alloys in order to enhance the thermoelectric properties in the heretofore unexplored cryogenic temperature range. While these studies are in their nascent stages, it is hoped that the understanding gained from using this approach will help one day to lead to useful Peltier coolers.

Chapter 3 Methodology

3.1 Synthesis

Sample preparations were different for each solid solution; therefore, a broad description of each of the methods used in this research is given below. Further details and any alterations to the process are discussed in the appropriate chapter for each solid solution.

3.1.1 Arc Melting

Stoichiometric quantities (unless otherwise noted in corresponding chapters) of pure elements were weighed out using a Mettler Toledo AL54 digital scale to within $\pm 0.0005\text{g}$ for each base compound of the solid solutions. The pure elements were obtained from Sigma Aldrich or Alfa Aesar, while some of the rare earth elements used in this research originated from Ames National Laboratory. The appropriate quantities of elemental pieces were then placed in the trough of a copper base, or hearth, for arc melting. Elements with higher vapor pressure and lower melting temperatures (such as Yb) were placed at the bottom of the trough and high melting temperature elements were arranged on top. This arrangement was implemented as an attempt to prevent vaporization and non-homogeneous losses. The arc-melting chamber was first evacuated via rotary pump and then backfilled to a positive pressure of 1-2atm with flowing argon gas. This pump and purge process was completed at least 5 times to ensure a pure argon environment for melting. A water-cooled tungsten electrode with a current of approximately 100 amperes was struck against the copper base to create an arc. This arc was then slowly passed over the raw elements in order to melt them together. After the molten piece cooled, the ingot was flipped and remelted. Any extraneous chunks that did not participate in the first melt were moved close to the large chunk and then melted together. After the preliminary melts in which all of the

elemental pieces were physically joined together, the ingot was flipped and re-melted four or more times in order to increase the diffusion process and encourage homogeneity within the ingot.

3.1.2 Homogenization

Some of the arc-melted ingots were not fully homogenized from multiple melts and therefore had to undergo a high-temperature heat treatment. The arc-melted ingots were broken into small chunks, or pulverized if possible, using pliers and/or a mortar and pestle. The resulting chunks/powders were loaded into an alumina crucible, which was sealed under vacuum in a carbon coated quartz tube. The quartz tubes were carbon coated by pyrolyzing a small amount of acetone in the bottom portion of the tube using a methane/oxygen torch. This torch was also used to seal the quartz ampoules while under a vacuum of at least 10^{-5} Torr. These tubes were then hung vertically in a Thermolyne 21100 tube furnace for a set temperature profile. Each material required different temperature profiles as will be discussed in the corresponding chapters.

3.1.3 Chemical Etching

Several of the samples were made by using an aluminum flux processing technique, similar to that used for single crystal growth [61,62]. In single crystals, the stoichiometric elements of the compound are melted within a flux material, which can be an element in the compound or an additional element that does not react with the elements in the compound. This process generally takes several days in which the elements are heated above the melting temperature of the flux and the desired compound and then slowly cooled to allow crystal growth. The flux material generally has a much lower melting temperature than that of the desired compound, thus as the sample is cooled the desired phase solidifies while the flux remains molten. After the crystal is grown, the sample is held above the melting temperature of the flux and the excess flux is

removed by centrifuging or chemical etching. In this study, the aluminum flux technique was used in an arc melter to achieve the desired phase in a polycrystalline sample rather than a single crystal grown in a furnace. Sodium hydroxide (NaOH) was found to react selectively with Al, while acting as an inert liquid to the desired phase, and was chosen as the chemical etchant. After arc melting, the ingot was broken into small chunks in order to increase the rate of penetration of 5M NaOH into the entirety of the ingot. These chunks were laid in a small plastic mesh bin to increase ease of access and drainage. Samples were left in the NaOH for at least 24 hours beneath a ventilation hood. After 24 hours, the sample chunks were rinsed in a series of distilled H₂O baths to remove all remnant NaOH. This process was determined to be complete once the pH level was 7 using pHDrion papers. The samples were then dried using a Thermolyne Hot Plate Oven at 100°C. The dried samples were then ground using an agate mortar and pestle. The powder was sieved through a 60mesh screen to remove any un-etched pieces. The un-etched sample was much more difficult to grind and therefore the two compositions (desired and un-etched) were very easy to separate physically. Un-etched pieces were returned to the NaOH bath for another 24 hours and the process was repeated. The sieved powder was then characterized and further processed to achieve the final sample.

3.1.4 Ball Milling

Some of the synthesis procedures, such as etching and high-temperature homogenization required that powder-processing techniques be used. Although some samples were dense and homogenous upon synthesis, all samples were powder processed in order to remain consistent. Samples were initially ground by hand using a mortar and pestle prior to undergoing ball milling. Stoichiometric quantities of each base compound were weighed out and then loaded and sealed with parafilm under argon into a stainless steel vial containing six stainless steel ball bearings;

two with diameter 0.5in and four with diameter 0.25in. Ball milling was done in a high-energy SPEX Sample Prep Mixermill 8000M vibratory mill. Milling times are reported in the following chapters. After ball milling, the sample was removed from the jar and passed through a 60mesh screen to remove any agglomerates. This ball milling process not only created well-mixed powders, but also reduced the particle size, and in some cases even caused mechanical alloying of the two compounds as established by x-ray diffraction (XRD).

3.1.5 Densification

Two different processes were used to densify the ball-milled powders. Primarily, pulsed electric current sintering (PECS), also known as spark plasma sintering, was used, however some samples were formed using traditional hot press methods. PECS processing was used because of its high temperature capabilities combined with short processing times [29]. During the PECS process, the sample powder is heated up within the die while pressure is applied and a current is simultaneously pulsed through the sample. This current causes very localized heating within the sample, which induces rapid sintering, making the densification process happen more quickly. Samples were pressed in a GT Advanced Technologies (formerly Thermal Technology LLC) SPS Model 10-4 system using a stainless steel rod in a graphite die while under an argon or vacuum atmosphere. Different compositions required varying time and temperature profiles that will be reported in the following chapters. Some samples were formed using hot pressing in order to compare results and as an attempt to increase the purity of the sample in which oxides were a problem. Further elaboration on the oxide impurities will appear in subsequent chapters. The hot press used was a Thermal Technology Model HP200-14020-23G, which also used a graphite die with a stainless steel rod under vacuum or argon. The only difference between hot pressing and PECS is that there is no current pulsed through the sample during hot pressing.

PECS generally resulted in higher density samples in less time, and was therefore the primary process used for densification of the samples reported in this work.

3.2 Characterization

While the primary focus of this thermoelectric research is to enhance the thermoelectric properties of materials at low temperatures, it is critical to know the composition and purity of the samples being measured. Without this information, it is impossible to draw conclusions about the different effects that occur in the materials because of the many variables that can influence thermal and electronic transport. Several characterization techniques are used to examine the density and purity of each sample made.

3.2.1 Density

The density of each sample disk was measured after powder processing and densification, using Archimedes' method. This method uses the mass of the sample in air (M_A), the mass of the sample in 200 proof ethanol (M_E), and the density of the ethanol (ρ_E) based on temperature (as obtained from Lange's Handbook of Chemistry, 10th edition [63]) to determine the sample density (ρ) in g/cm³.

$$\rho = \frac{M_A}{|M_A - M_E|} \rho_E \quad \text{Equation 13}$$

This measured value can be compared to the theoretical value for the given composition in order to determine the percent density of the sample. The theoretical density can be obtained from literature or calculated for each sample if the lattice parameter(s), mass of atoms and unit cell structure are known. All samples that were studied for their thermoelectric properties had measured densities of at least 95% of theoretical value.

3.2.2 X-ray Diffraction

Powder x-ray diffraction (XRD) was the main characterization technique used to identify phase purity in samples. XRD was conducted using a Rigaku MiniFlexII Benchtop system using Cu K α radiation. Patterns were collected on each sample following every step in the synthesis process. These patterns were then compared to existing powder diffraction files in the Jade9 database. X-ray diffraction is considered a reliable method for detecting crystalline phases of greater than three atomic percent of the total composition. It is possible to have secondary phases in a sample that do not appear in the patterns but may affect the electronic properties or appear in other characterization methods if this phase is only a small fraction of the total composition or exists in an amorphous state. XRD patterns were used not only to detect impurity phases in the samples, but also to calculate the lattice parameter. The plane corresponding to each peak was indexed and using the d-spacing and the crystal structure, the lattice parameter(s) could be calculated. These lattice parameters are important for comparing the average valence with the size of the unit cell.

3.2.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to find the average grain sizes of densified samples and to identify any impurity phases that could be observed. The microscope was a JEOL JSM-6610LV from JEOL Ltd. Tokyo, Japan. Secondary electron images reported here show fractured surfaces for different samples. While fractured surfaces are not ideal for measuring grain sizes, this method proved most convenient and allowed for a rough approximation of the average grain size. Backscatter mode was used to observe differences in the average atomic weight, indicating areas of the sample that have different atomic composition. While these images were gathered to qualitatively identify impurity phases, they are not reported in this work. Finally, the different elements in the sample were mapped using energy dispersive x-ray

spectroscopy (EDS) using an Oxford Instruments Aztec system, software version 2.1a, using a 20mm² silicon drift detector crystal and an ultrathin window. The resulting patterns were again used to qualitatively and semi-quantitatively identify the elements that made up the different phases but are not published in this report.

3.3 Property Measurement

3.3.1 Transport Properties

Measurement of the three thermoelectric transport properties (electrical resistivity $\rho = 1/\sigma$, the Seebeck coefficient S , and thermal conductivity κ) was performed from 80 to 350 K under vacuum in a Janis model ST-100 liquid nitrogen flow cryostat. Electrical resistivity was measured with an uncertainty of approximately 3% using a four-probe DC technique. The Seebeck coefficient and thermal conductivity are measured using a steady state technique in which a small metal film resistor is affixed at one end of the sample while the other end attached to a copper base which is then anchored to the cryostat cold tip. When this resistor is energized, heat flows down the sample and a steady state temperature difference is developed, which is sensed by a pair of copper-constantan thermocouples. These thermocouples are soldered to copper contacts which are attached to the sample using a silver epoxy. The resistor is externally wrapped in a copper foil to provide an electrically conductive pathway at the top of the sample. The electrical conductivity is measured by passing a current through the sample and measuring the voltage difference at the thermocouples. A schematic of this sample measurement configuration is shown in Figure 3-1. From this, the lattice thermal conductivity can also be determined by simple subtraction. All contacts to the sample are made using silver epoxy, and thermal and electrical voltages are sensed using Keithley multimeters. From a set of measurements on standards it was determined that this method gives an uncertainty in both

Seebeck coefficient and thermal conductivity of approximately 5%. The Wiedemann-Franz law, as previously described, was used to calculate the electronic contribution to the thermal conductivity.

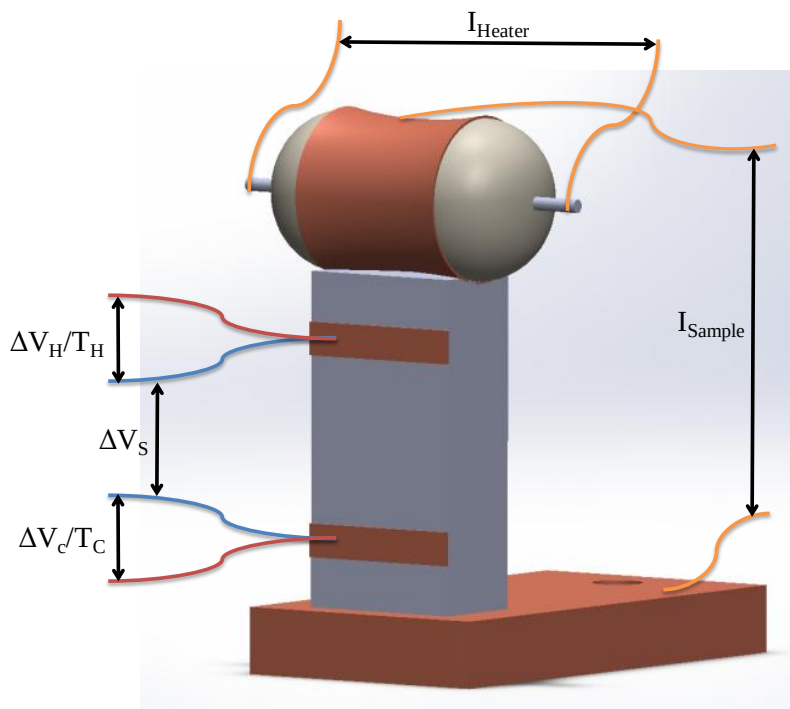


Figure 3-1: Sample mounting configuration for transport property measurements

Transport property measurements were extended down to 2K by colleagues at Ohio State University using the thermal transport option (TTO) in a Physical Properties Measurement System (PPMS) by Quantum Design. The results of this technique return similar accuracies as that of the nitrogen flow cryostat reported above.

3.3.2 Magnetic Properties

To assist in the identification of the valence state of Yb, magnetization measurements were performed on some of the samples. The magnetic susceptibility of select samples was determined by measuring the magnetic moment of the sample in a Quantum Design superconducting

quantum interference device (SQUID) magnetometer in the Physics and Astronomy Department at MSU. The moment was collected in a magnetic field of 5000 gauss from 2K to 300K. Small pieces (typically <0.5g) were placed inside of a small plastic pouch and then slid into a plastic straw. The straw was inserted into the SQUID chamber that was then evacuated and cooled to 2K. Thermal equilibrium was achieved by allowing the sample to sit at each temperature point for approximately 15 minutes before the magnetic moment was measured.

The magnetic data collected on these samples had to be corrected for oxide impurities found in the samples. This oxide phase contributed a paramagnetic signal that overwhelmed the very low temperature features in the data. This impurity signal could be removed by calculating the quantity of impurity by fitting the low temperature (2-10K) Curie tail from the inverse moment versus temperature data to a line and subtracting it from the magnetic moment. Doing so left a magnetic susceptibility curve with a peak at low temperatures, characteristic of intermediate valence compounds.

After correction, this data was analyzed using the interconfigurational-fluctuation (ICF) model, proposed by Sales and Wohlleben [40]. This model is used to fit the magnetic susceptibility curve for Yb-based materials using two variables, the excitation energy, and the spin fluctuation temperature. By fitting these two variables to the data, the average Yb valence was extracted as a function of these variables. This information allowed for a direct comparison the average Yb valence and the other data collected, including the Seebeck coefficient.

Chapter 4 YbAl₃-Based Solid Solutions

4.1 Introduction

Yb-based compounds are very interesting for low temperature thermoelectric research due to their large power factors at and below room temperature. One of the most well known Yb-based materials is YbAl₃, because it has the largest power factor reported for any bulk material at room temperature [23,64–66]. This large power factor is a strong impetus to further study and pursue YbAl₃ as a potential thermoelectric material. While the thermoelectric properties have been measured by many groups [64,65,67–69], minimal experimental work has been done to optimize these thermoelectric properties. This is primarily due to the difficulty in obtaining large single crystals of this compound, and synthesis of large polycrystals has gone essentially uninvestigated. The large thermal conductivity in this compound must be reduced in order to take advantage of the advantageous power factor. A simple but common approach to reduce this thermal conductivity is via solid solution formation [25,31], taking advantage of the aforementioned scattering of phonons by substituting atoms of differing masses.

First-principle calculations have shown that there are many isostructural alloys that could be synthesized as full solid solutions with YbAl₃. Substitution on the Al site could come in the form of Mg, Cu, Zn, In and Sn [70] while Ho, Er, Tm [71], Sc [72] and Lu [72,73] could be substituted on the Yb site. There is also a vacant octahedral site in the cubic structure that could be filled with a small atom such as Mn, as was reported by He et al. [67]. Magnetic properties have been collected on several of these alloys, revealing strong changes in the magnetic susceptibilities as the Yb atoms are diluted. The low-temperature peak in the magnetic susceptibility, which is characteristic of intermediate valence systems, is reduced and shifted

toward higher temperatures in both Lu [74] and Sc [72] substituted systems. These changes in magnetic susceptibility indicate a change in the Yb valence and suggest the Seebeck coefficient may be dramatically altered, although the Seebeck coefficient is not reported in the literature for these compositions. The work described in this section investigates the effects of Sc, Er, and Lu substitution on the thermoelectric properties of YbAl_3 and has been published in *Intermetallics* and the *Journal of Electronic Materials* [75,76]. Attempts were also made to form solid solutions with In and Sn substituting for Al; however, no phase pure compounds were successfully synthesized and thus could not be reported.

YbAl_3 has a cubic crystal structure [77–80], as shown in Figure 4-1, which is relatively simple in structure therefore has a very large lattice thermal conductivity. In order to reduce this thermal conductivity, solid solutions are formed to introduce defects into the lattice and scatter phonons. The three alloys investigated here are isostructural to YbAl_3 and thus form complete solid solutions. The synthesis procedure for each family of compounds was quite complex and will be discussed in the following section. In order to overcome obstacles in the synthesis, solid

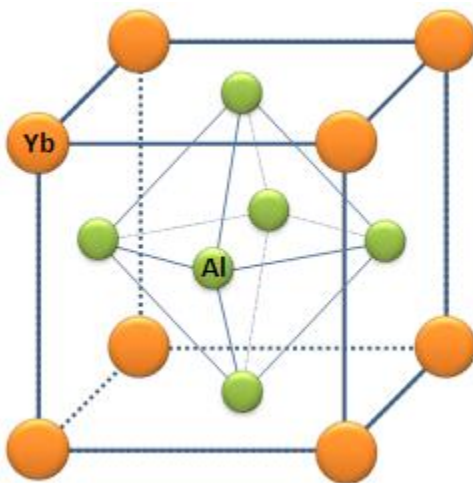


Figure 4-1: Unit cell diagram of YbAl_3 .

solutions were formed by first creating the individual binary compounds (YbAl_3 , ScAl_3 , ErAl_3 , and LuAl_3) and then using powder processing to create compounds of varying compositions.

4.2 Pure YbAl_3

4.2.1 Synthesis

The nominal composition YbAl_3 was arc melted in order to achieve an Al rich environment and encourage the growth of the YbAl_3 phase. A peritectic reaction is shown in the phase diagram [79], see Figure 4-2, indicating that stoichiometric YbAl_3 forms from two separate phases, solid YbAl_2 and liquid $\text{YbAl}_3 + \text{Al}$, upon cooling. As discussed in previous studies [64,65,81,82], this YbAl_2 phase is unavoidable by simply arc melting stoichiometric quantities. Assuming perfect stoichiometry was maintained during the arc melting process, a prolonged heat treatment at just below the peritectic temperature would allow for the homogenization of the YbAl_3 phase.

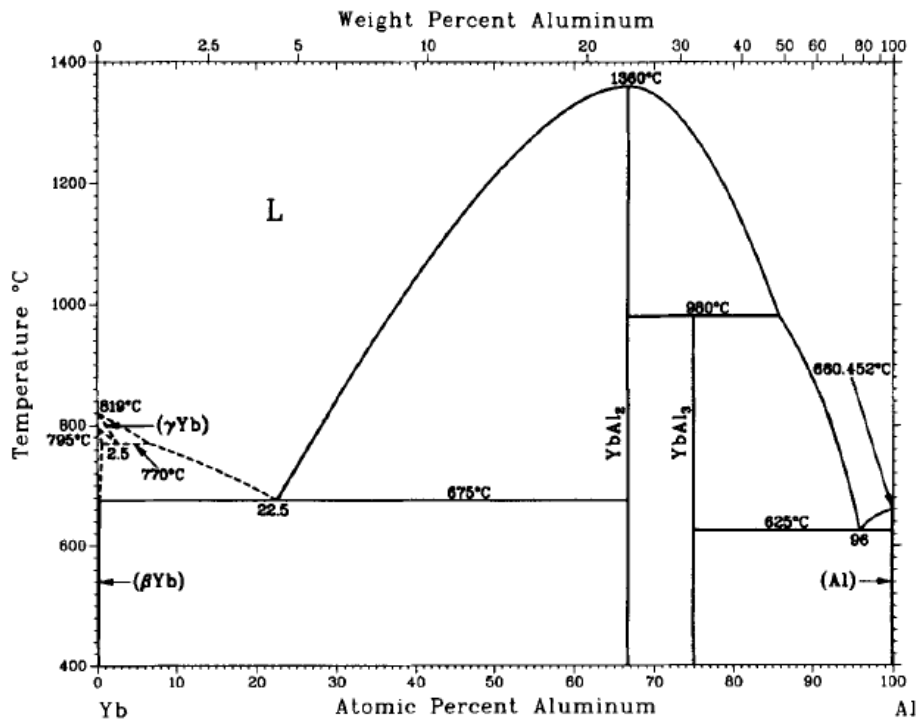


Figure 4-2: The Ytterbium-Aluminum binary phase diagram by Gschneider and Calderwood [79].

However, this is an extremely slow diffusion process as the YbAl_2 phase has already crystallized at this temperature and is not a realistic synthesis procedure. Thus, an Al rich environment was created to force the compound to maintain the YbAl_3 phase without allowing YbAl_2 to form. This approach of using an Al rich environment is commonly found in the literature for growing single crystals [65,68,73,74,82,83], however, it is a novel approach to use a flux while arc-melting for bulk polycrystalline samples.

After arc-melting in the aluminum rich environment the sample was then etched in NaOH as previously described in Section 3.1.3. This etching process removed all of the excess Al from the sample, leaving only the desired YbAl_3 phase, which was then easily powdered. Etching with NaOH is also done in single crystal growth; however, the nature of single crystals prevents the excess Al being incorporated into the bulk and is only found on the surface, and therefore does not require breaking the single crystals into smaller pieces.

The powder resulting from the etching step was then ball milled for 40 minutes. Densification was done using PECS at 800°C for 30 minutes under 60 MPa of pressure in an argon atmosphere. Several different approaches were taken to densifying these samples in an attempt to reduce the oxide phase that formed during sintering. Samples were processed using shorter pressing times, lower temperatures, and under vacuum rather than argon; however none of these precautions improved the quality of the samples. Hot pressing, rather than PECS, also proved futile in an attempt for higher purity samples.

4.2.2 Characterization

YbAl_3 forms in the Cu_3Au or L1_2 crystal structure, which is a cubic structure with Yb on the corners and Al on the faces as previously shown in Figure 4-1. XRD was used at each step in the

synthesis procedure to determine the phases present in the sample and ensure consistency throughout many batches. Figure 4-3 demonstrates the XRD patterns that result from a single batch of YbAl_3 at each step in the processing chain. The arc melted nominal YbAl_9 composition (Figure 4-3A) shows the characteristic peaks of YbAl_3 in addition to peaks corresponding to pure Al metal indicated by *, as expected from the Al rich arc-melting environment. After etching, the powder shows sharp peaks representative of only the desired YbAl_3 phase (Figure 4-3B). After ball milling the pattern does not show any additional peaks, however the characteristic peaks are broadened (Figure 4-3C). This broadening could be a result of several factors including reduced

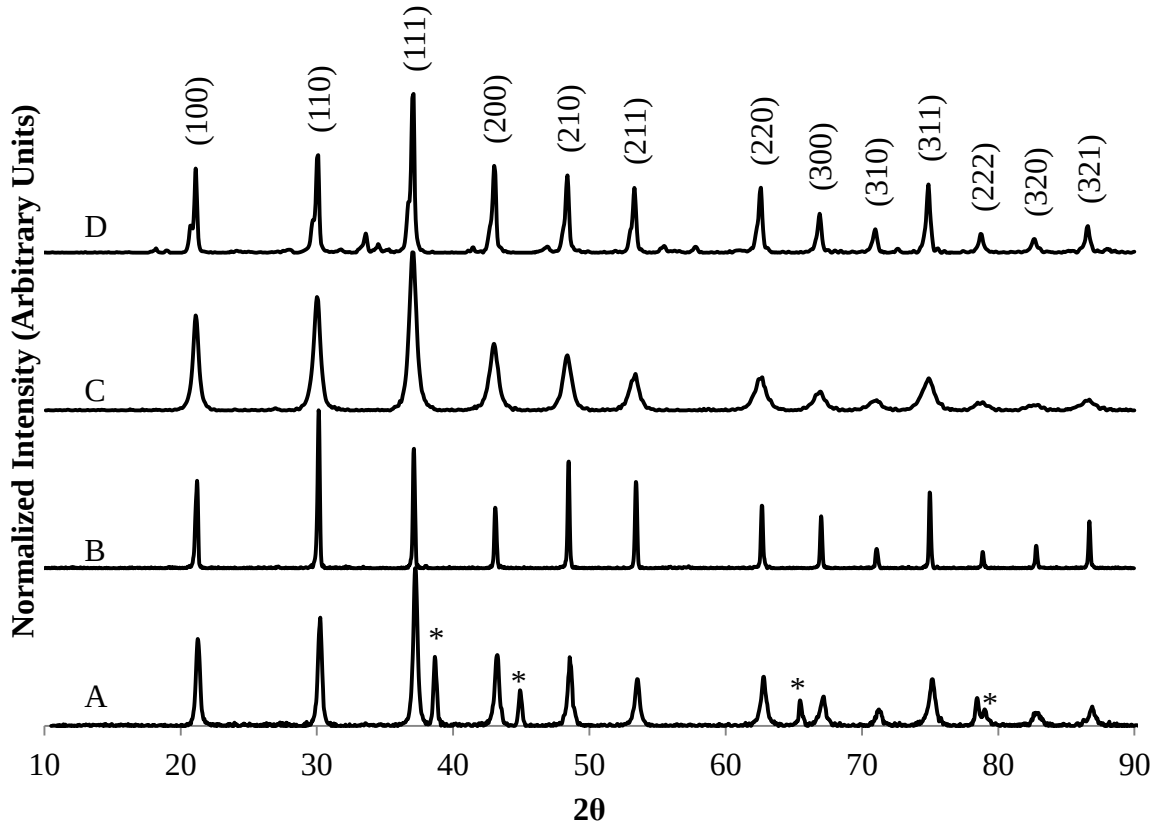


Figure 4-3: XRD patterns of each step in the YbAl_3 synthesis process as labeled: A) after the nominal YbAl_9 was arc melted - * indicate peaks from the pure Al phase, B) after sample is etched in NaOH to remove excess Al, C) after YbAl_3 is ball milled, D) after densification using PECS – unlabeled peaks are oxide impurity phase.

particle size, defects in the crystal structure such as dislocations, point defects or concentration gradients, and finally strain, which may occur from the high energy ball milling process. After densification, the peaks narrow again (Figure 4-3D), suggesting grain growth, reduced strain and/or homogenization of the crystal structure during the sintering step. The XRD pattern also reveals several un-desired peaks that can be indexed to a Yb-oxide phase. The oxide phase was resilient to several different synthesis techniques and the samples were used as the baseline for the solid solution.

4.2.3 Transport Properties

The thermoelectric properties of YbAl_3 have been reported in several different papers [64,65,67,83], each showing very large power factors. The data collected in this work is consistent with the literature data, and is reported in each of the sections below for comparison for the solid solutions.

4.3 $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$

The scandium atom is ideal for creating a solid solution because although it forms the isostructural compound ScAl_3 , there is a large mass mismatch between Sc and Yb [72,73,80]. A full solid solution of $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$, where $x=0, 0.25, 0.50, 0.75$, and 1.0 , was created to study the effects of the solid solution on the lattice thermal conductivity and overall thermoelectric figure of merit.

4.3.1 Synthesis

The YbAl_3 base compound was synthesized as described above, separately from ScAl_3 . According to the phase diagram[84] shown in Figure 4-4, the ScAl_3 phase forms congruently and thus the stoichiometric quantities of Sc and Al were arc melted. The resulting ingot was then

powdered and heat-treated for 24 hrs at 900°C to ensure homogeneity. The arc melted sample showed no obvious signs of phase separation or impurities. Stoichiometric quantities of YbAl₃ and ScAl₃ were then ball milled together for 40 minutes, sieved, and densified. PECS processing was done for 30 minutes at 800°C under 60MPa pressure in an argon atmosphere.

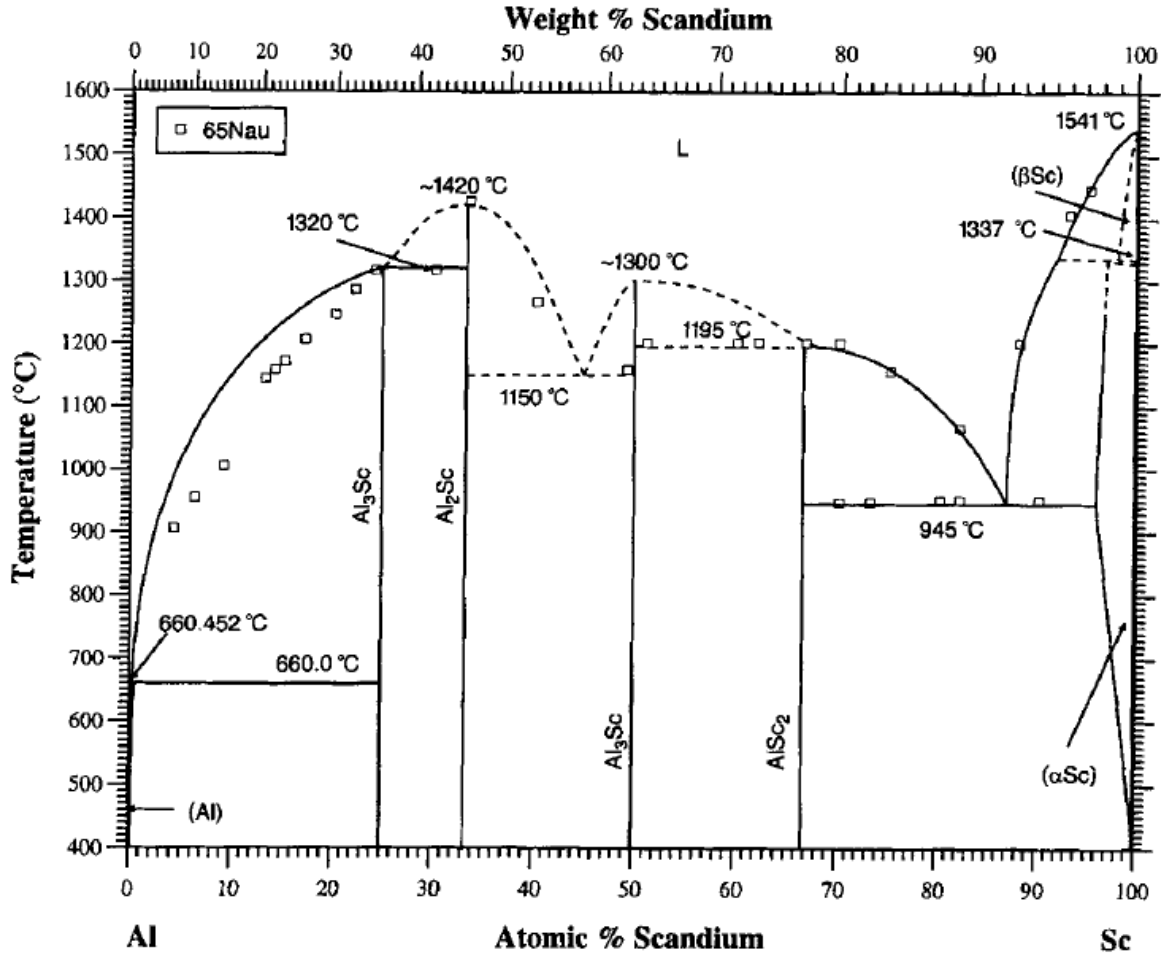


Figure 4-4: The Sc-Al phase diagram showing the congruent melting of the ScAl₃ phase [84].

4.3.2 Characterization

Figure 4-5 shows the single phase XRD patterns from the Yb_{1-x}Sc_xAl₃ solid solution with minor oxide impurities, consistent with those observed in the pure YbAl₃ samples. These XRD patterns

also indicate that the oxide impurity phase is reduced as Sc is increased in the system, indicating that Yb has a higher tendency to oxidize in lower oxygen content environments than Sc. Majewski et al. reported that single-phase samples were not achieved for compositions $0.5 < x < 1.0$. However, the entire range of concentrations $x = 0, 0.25, 0.50, 0.75$, and 1.0 were successfully synthesized in this work, except for a minor Yb-oxide impurity phase. The patterns in Figure 4-5 show that the crystal symmetry is not altered by the addition of Sc into the YbAl_3 system; however, the lattice parameter is affected as expected from isostructural alloying. The XRD patterns show a shift in the peaks toward larger angles, indicating that as the Sc concentration is increased, the lattice parameter is reduced. This can be more clearly seen by calculating the lattice parameter from these peaks and plotting versus Sc concentration, and is displayed in Figure 4-6. Literature data for $0 \leq x \leq 0.90$ [72] and $x=1.0$ [80] are represented by the closed circles and show good agreement with the lattice parameters calculated in this study.

The end compounds of this solid solution ($x = 0$ and 1.0) were investigated via SEM. Secondary electron images in Figure 4-7 show grain size to be on the order of several microns. EDS maps of the sample, not included here, also qualitatively confirmed the oxide impurity phase that was identified by XRD.

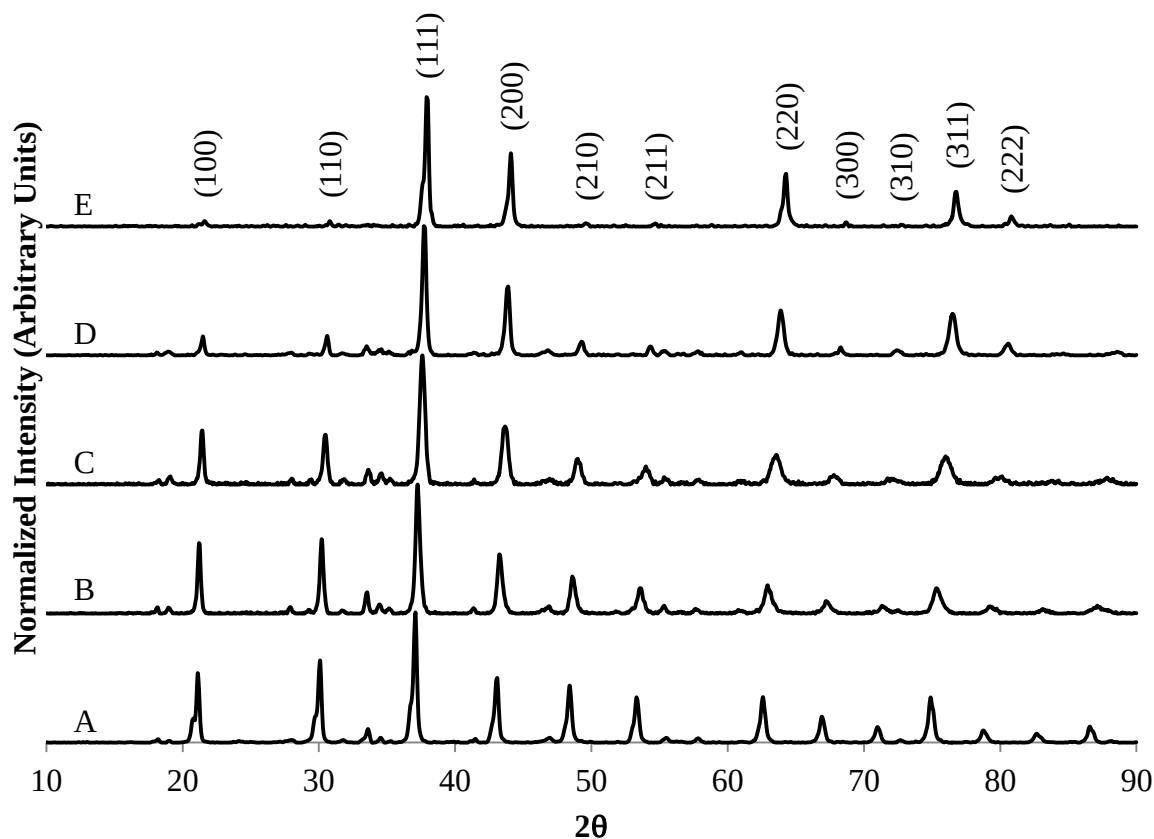


Figure 4-5: XRD pattern for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where A) $x = 0.0$, B) $x = 0.25$, C) $x = 0.50$, D) $x = 0.75$, E) $x = 1.0$ – unlabeled peaks are from the oxide impurity phase.

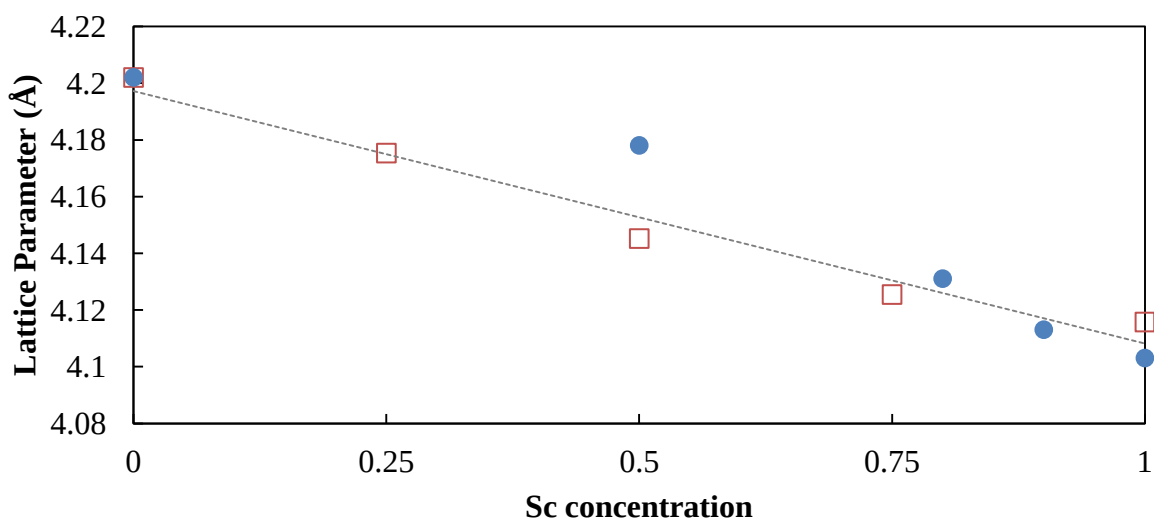


Figure 4-6: Lattice parameters for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $0 \leq x \leq 1$ at room temperature. Closed symbols come from literature data [79, 81].

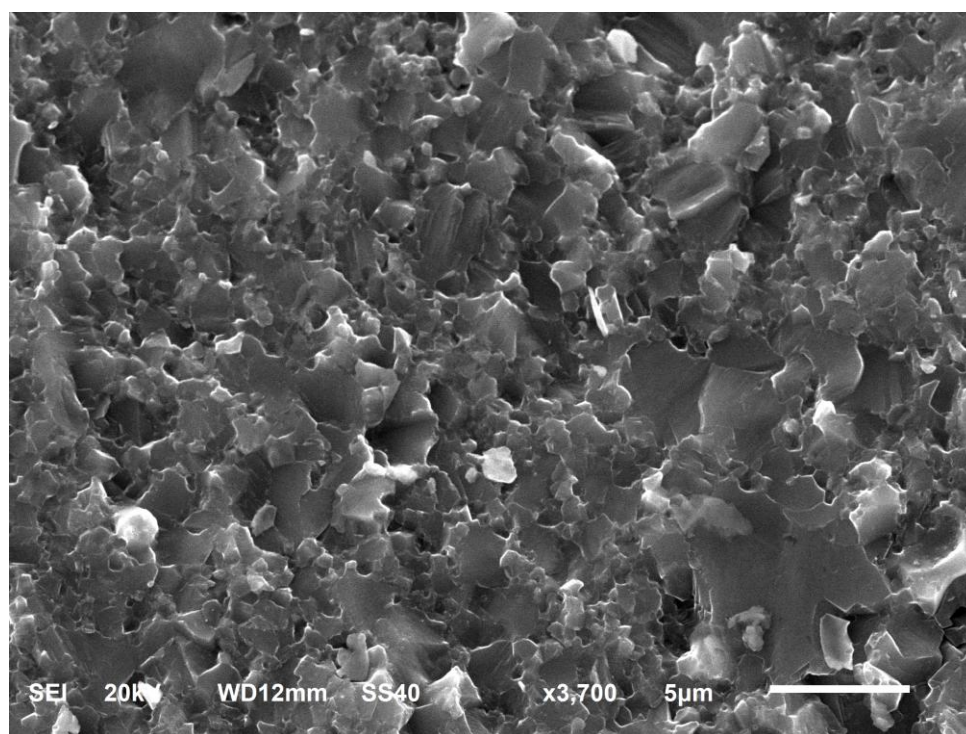
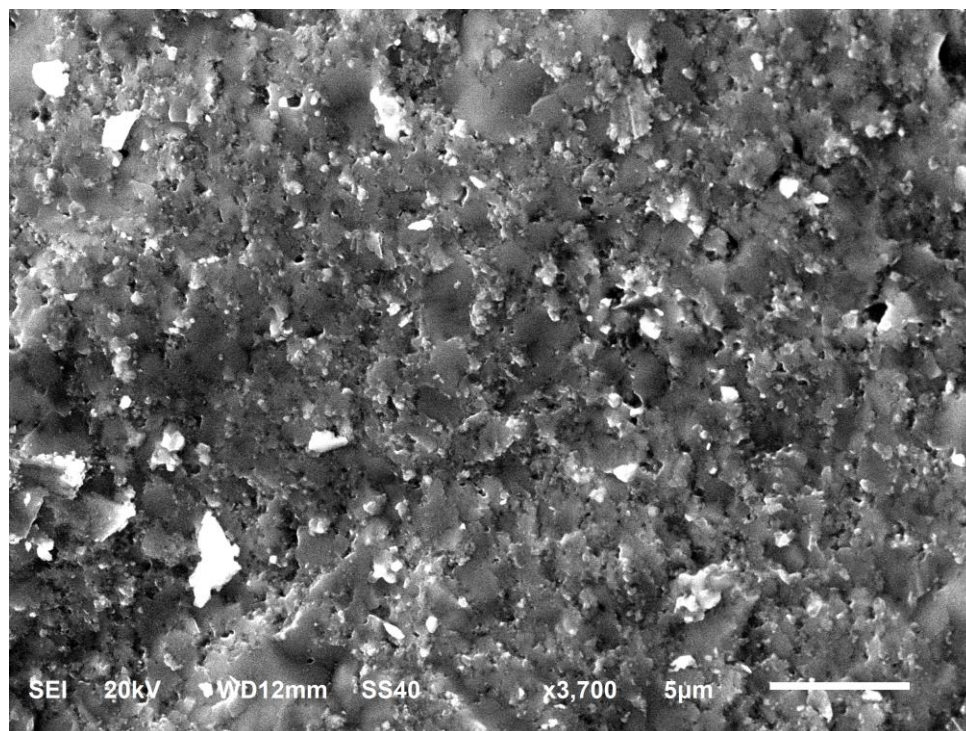


Figure 4-7: SEM images of fractured surfaces for A) YbAl_3 and B) ScAl_3 .

4.3.3 Transport Properties

The thermoelectric transport properties were measured on each sample in the solid solution using the techniques described in Section 3.3.1. While the primary purpose of creating a solid solution was to reduce the lattice thermal conductivity, strong changes were also observed in the electronic properties. As shown in Figure 4-8, the electrical resistivity of the YbAl_3 sample rapidly increases from low temperatures until approximately 300K where the curve plateaus. The trend and magnitude of the resistivity for this sample closely matches reported values in the literature by Rowe et al [83]. The addition of scandium causes the resistivity to decrease greatly and display a more linear temperature dependence. In fact, the resistivity of the pure ScAl_3 sample is comparable to that of many good metals, at approximately $11 \mu\Omega\text{cm}$ at room temperature.

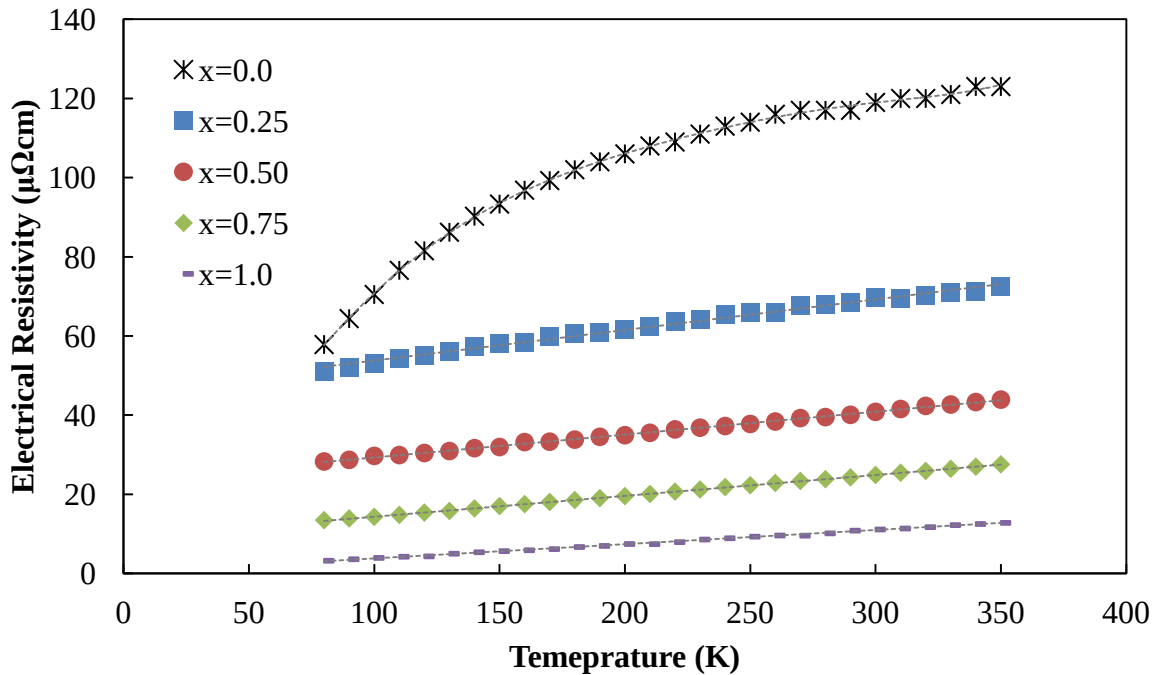


Figure 4-8: Electrical resistivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.5, 0.75$, and 1.0 . Dashed lines are guides to the eye.

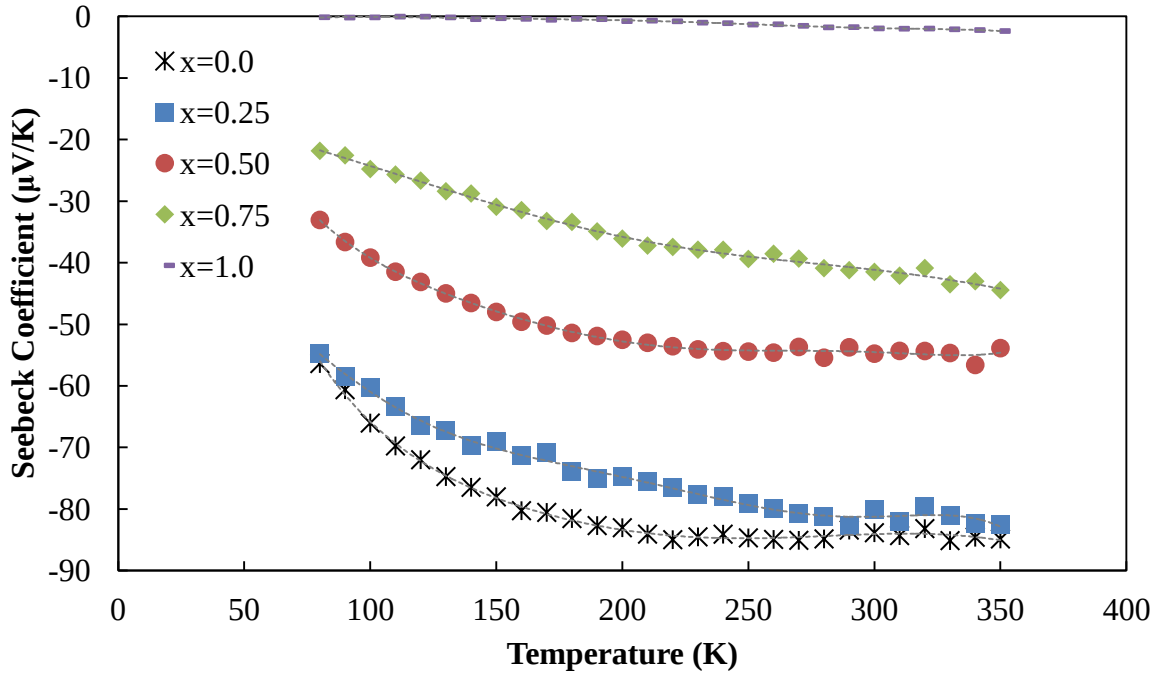


Figure 4-9: Seebeck coefficient from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.5, 0.75$, and 1.0

Figure 4-9 shows a Seebeck coefficient for YbAl_3 that is consistent with other bulk polycrystalline samples reported by Rowe et al. [83]. This Seebeck coefficient decreases as Sc concentration increases. However, this reduction in the Seebeck coefficient does not occur as rapidly as the reduction in electrical resistivity, particularly for the $x=0.25$ composition which is barely altered. However, at the $x=1.0$ composition, the Seebeck coefficient is essentially zero, which is again characteristic of a good metal. The rapid reduction in the electrical resistivity and the relatively slow reduction of the Seebeck coefficient with respect to Sc concentration results in significant enhancements in the power factor. The power factor is increased across the entire temperature range for the $x=0.25$ composition, while the $x=0.50$ and 0.75 compositions show moderate enhancements in the power factor above 130K and 200K respectively, as shown in Figure 4-10.

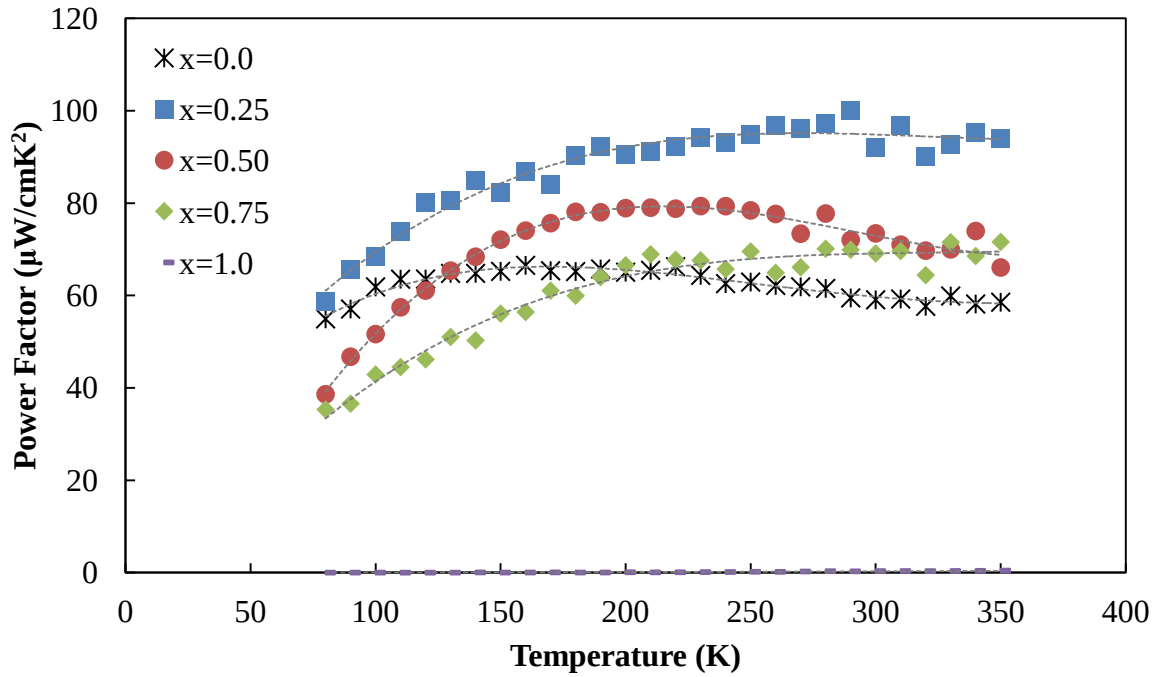


Figure 4-10: Power Factor from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0 .

The purpose of creating a $\text{YbAl}_3\text{-ScAl}_3$ solid solution is to take advantage of the mass mismatch between Yb and Sc, in order to reduce the lattice thermal conductivity. The difference between the atomic masses of Yb (173.05amu) and Sc (44.96amu) should cause a large increase in the phonon scattering rate, according to Equation 12. The nearly metallic resistivity results in a very large electronic component to the thermal conductivity that grows rapidly as the electrical resistivity is dramatically reduced with increasing Sc content. However, the lattice thermal conductivity is reduced for $x=0.25, 0.50$, and 0.75 , creating an opposing effect on the total thermal conductivity. Figure 4-11 shows that the total thermal conductivity is increased for all concentrations of scandium because the reduction in the lattice thermal conductivity is not large enough to counteract the increase in the electronic component. Fortunately, the increase in thermal conductivity is very minimal in the $x=0.25$ sample.

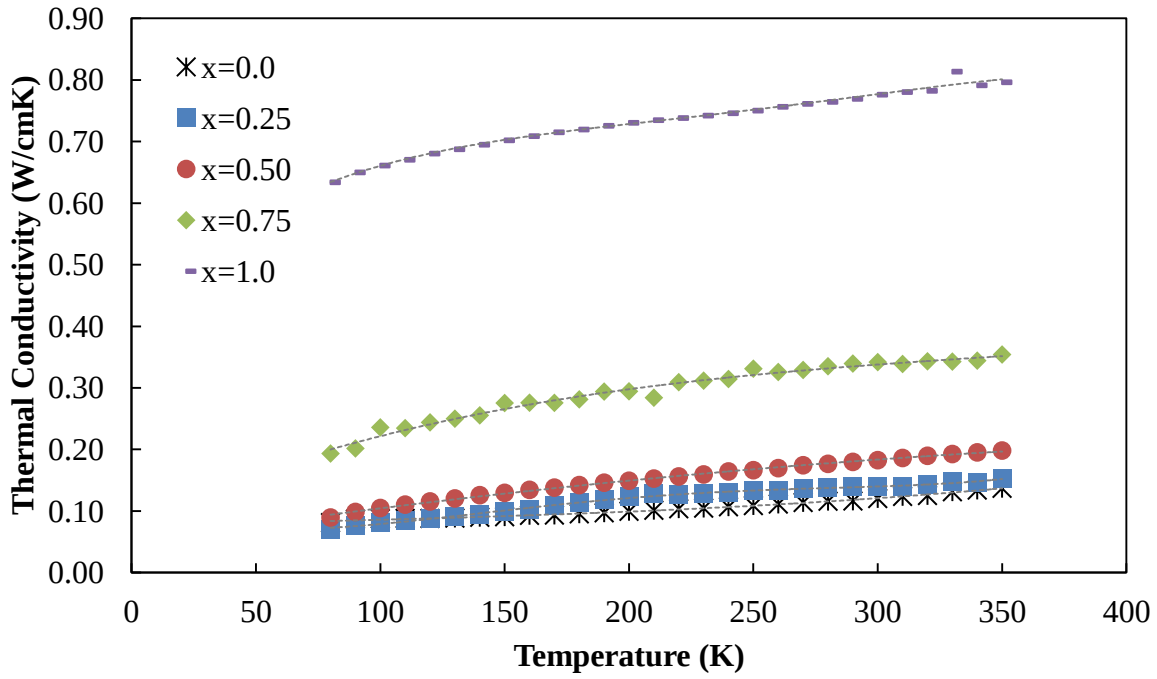


Figure 4-11: Total thermal conductivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0 .

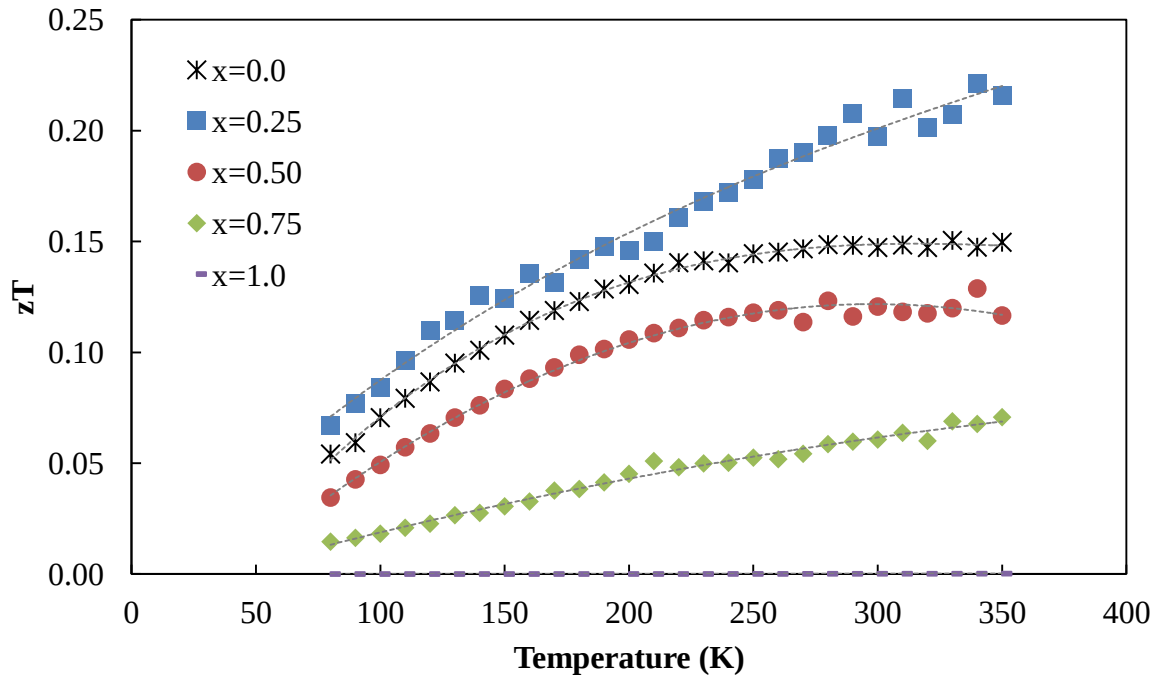


Figure 4-12: Dimensionless figure of merit from 80K to 350K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0 .

The enhanced power factor in combination with the minimally increased thermal conductivity of the $x=0.25$ sample results in an overall enhancement of the zT over the entire temperature range. As can be seen in Figure 4-12, the zT is increased by nearly 40% at room temperature. This is a significant improvement to this widely studied low-temperature thermoelectric material. Unfortunately, while the large electrical conductivity allows for a very large power factor, this conductivity also contributes to the large thermal conductivity, which is the limiting factor in further improving the thermoelectric efficiency of this material.

4.4 $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$

While Sc was an ideal element for reducing lattice thermal conductivity because of the large mass mismatch, it also strongly affected the electronic properties. The Seebeck coefficient and resistivities became more metallic as Sc was added. Another substitutional atom with a small mass mismatch but more similar electronic properties is erbium. Erbium also forms the isostructural compound ErAl_3 that is used to create a full solid solution. No experimental work on the YbAl_3 - ErAl_3 system was found in the literature; however, first-principle calculations show that a full solid solution between these two compounds is possible and the electronic structure should not be significantly altered [71].

4.4.1 Synthesis

Similarly, to the Yb-Al phase diagram, ErAl_3 shown in Figure 4-13 [85] also undergoes a peritectic reaction and therefore an Al rich environment is necessary to achieve a phase-pure sample. The same synthesis technique of arc melting, etching and powder processing, as described for the YbAl_3 compound was utilized to synthesize ErAl_3 , this time using the nominal composition ErAl_5 . A full solid solution of $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ was synthesized for $x=0.0, 0.25, 0.50, 0.75$, and 1.0 .

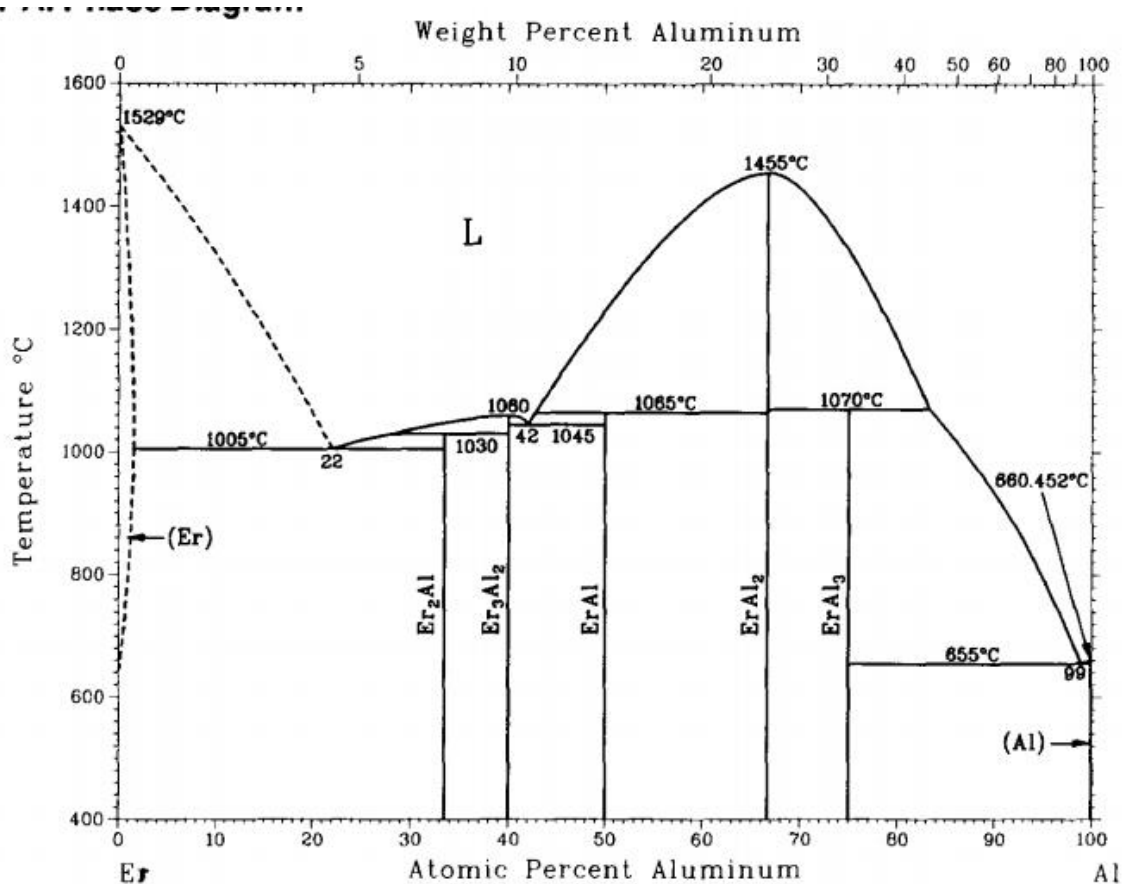


Figure 4-13: The Erbium-Aluminum binary phase diagram by Gschneider and Calderwood [85].

4.4.2 Characterization

The XRD patterns clearly show the L1 crystal structure for the densified samples for all compositions. The shift in the characteristic XRD peaks is significantly smaller than that of the Sc samples, because Er is much closer in size to Yb than Sc, so the lattice parameter is not significantly altered. The XRD patterns shown in Figure 4-14 reveal that there is an abrupt and dramatic increase in the oxide phase of the $x = 0.75$ and 1.0 samples. While it is believed that the role of this oxide impurity phase is minimal for low Er concentration samples, it is likely the transport properties are influenced by the impurity phase in the $x = 0.75$ and 1.0 samples. The

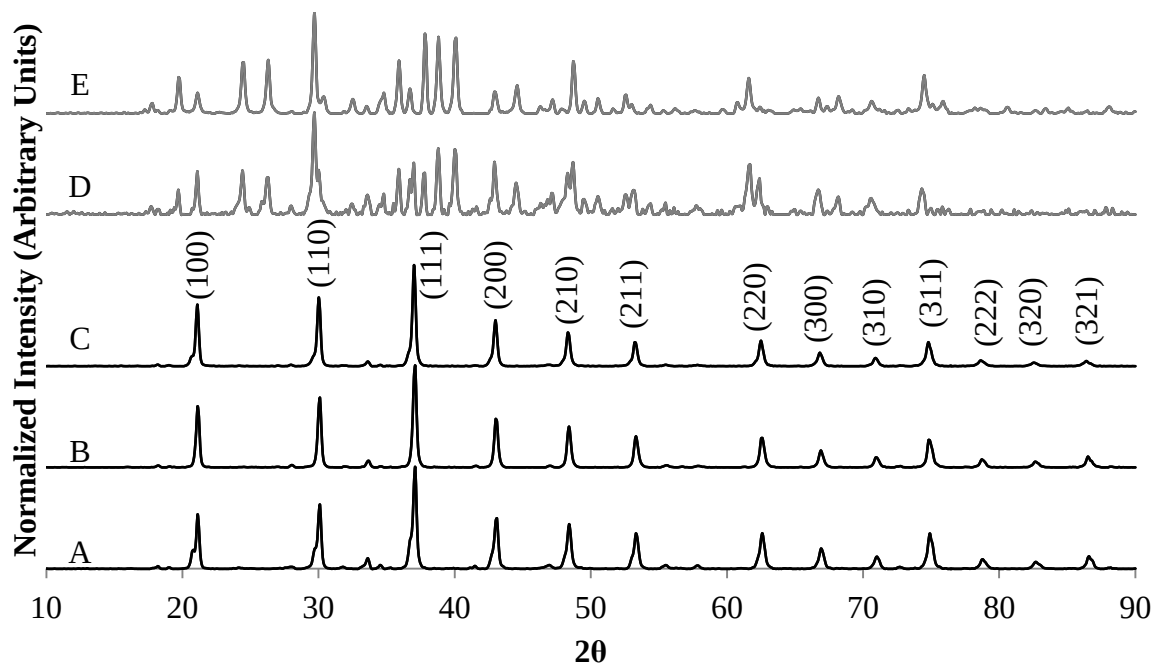


Figure 4-14: XRD pattern of the Yb_{1-x}Er_xAl₃ solid solution at room temperature where A) x = 0, B) x = 0.25, C) x = 0.50, D) x = 0.75, and E) x = 1.0.

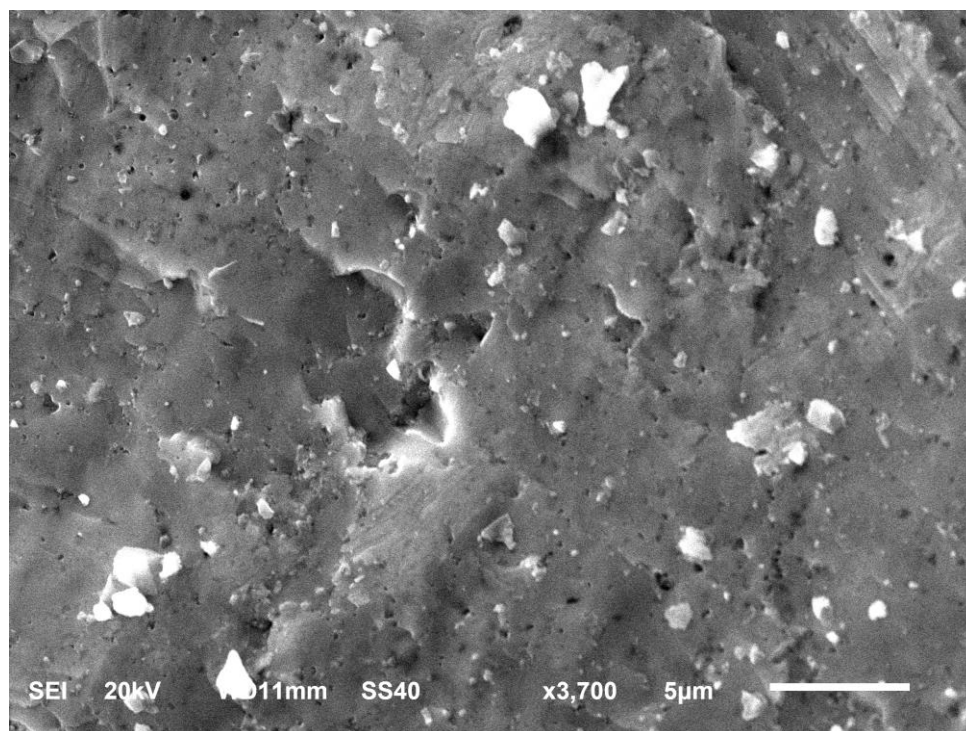


Figure 4-15: SEM images of fractured surfaces for ErAl₃.

thermoelectric properties were measured on these samples, but they reflect this higher-than-normal oxide phase and are not reported in all cases.

Figure 4-15 shows the SEM micrograph for the ErAl_3 fractured surface. This micrograph shows a larger grain structure than that of YbAl_3 and ScAl_3 ; however, grains are still on the order of several microns in diameter.

4.4.3 Transport Properties

The electrical resistivity of the samples was strongly decreased by the addition of Er. However, samples with Er concentrations $x=0.75$ and 1.0 had higher than expected electrical resistivity, as shown in Figure 4-16, which is suspected to arise from the large insulative oxide phase that appears in the XRD patterns. For this reason, the transport properties of these two compositions are not associated with phase pure samples and not reported for the rest of the thermoelectric properties.

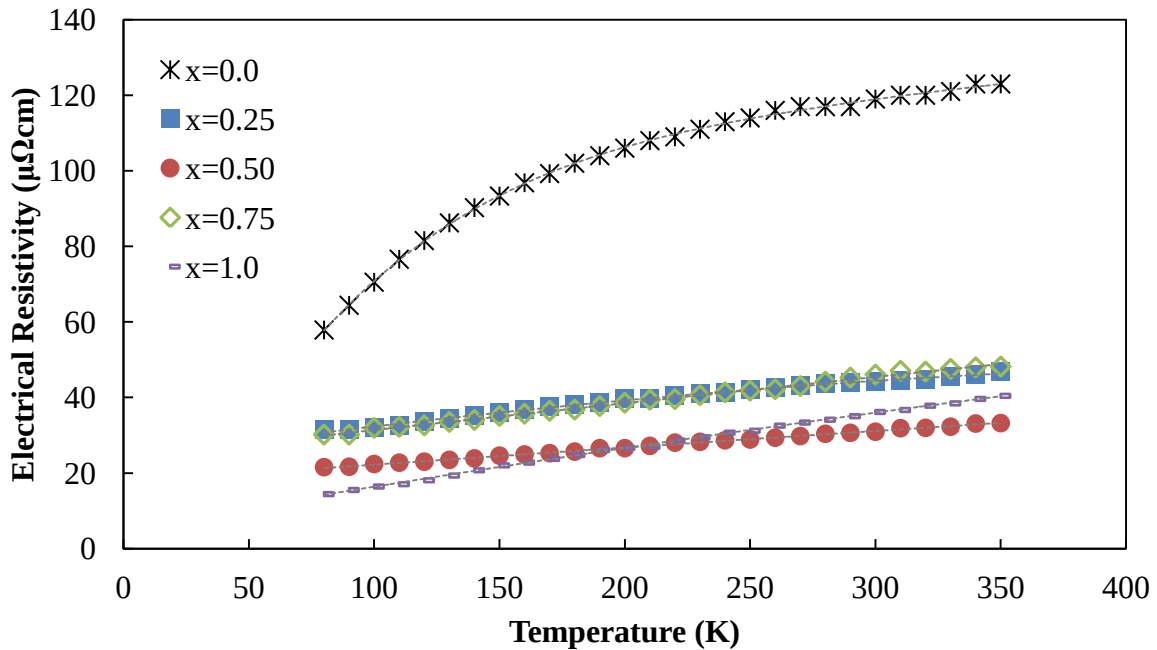


Figure 4-16: Electrical resistivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0 .

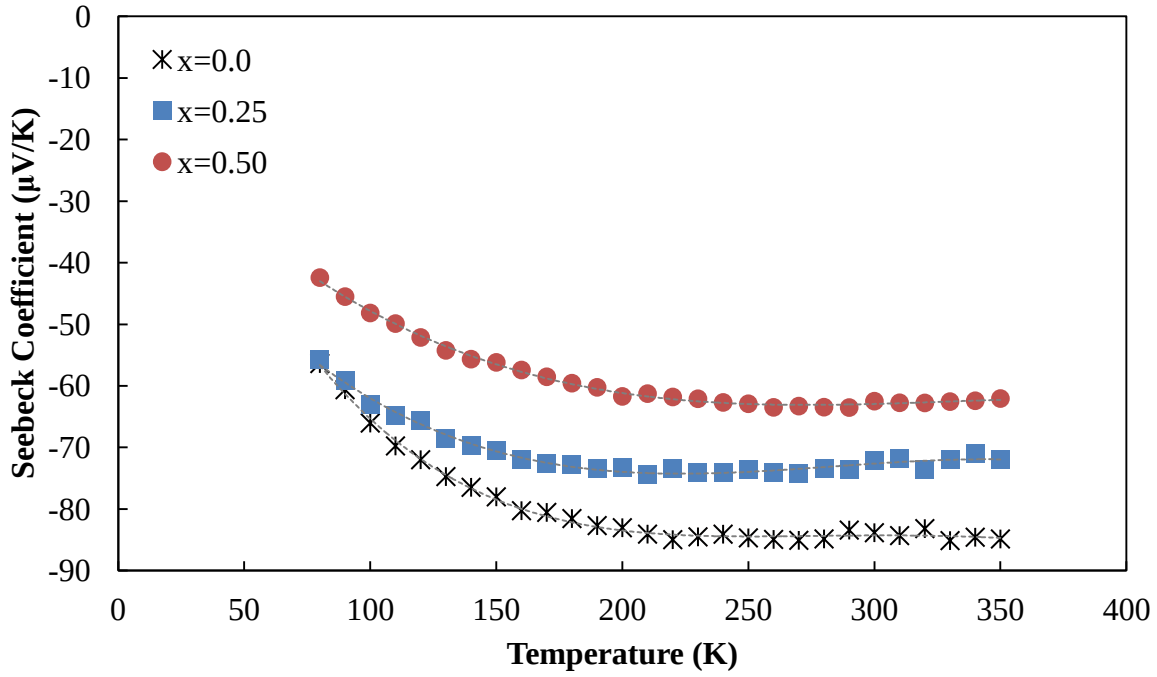


Figure 4-17: Seebeck coefficient from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25$, and 0.50 .

Figure 4-17 shows that the Seebeck coefficient was also reduced with the addition of Er into the system, but not as strongly for the $x=0.50$ sample as occurred in the Sc substituted $x=0.50$. This rapid decrease in the electrical resistivity and small drop in the Seebeck coefficient results in a gigantic power factor value of nearly $140 \mu\text{W}/\text{cmK}^2$ between 120K and 300K for both the $x=0.25$ and 0.50 samples. Figure 4-18 shows that Er substitution nearly doubles the original YbAl_3 power factor.

With a very promising power factor, the thermal conductivity of these samples is of utmost importance. The reduction to the lattice thermal conductivity is not expected to be very large in comparison to the Sc substituted samples because the mass difference between Er and Yb is quite small. However some reduction in the lattice component is revealed above 150K and

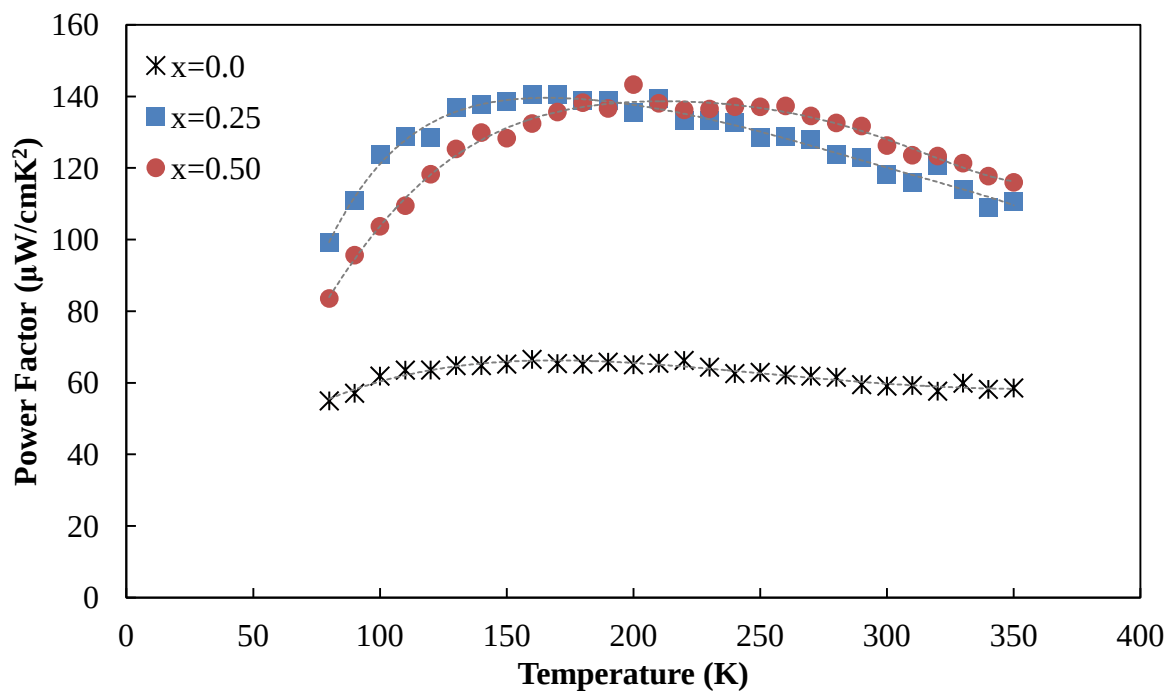


Figure 4-18: Power factor from 80K to 350K for the solid solution $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ where $x = 0.0, 0.25$, and 0.50 .

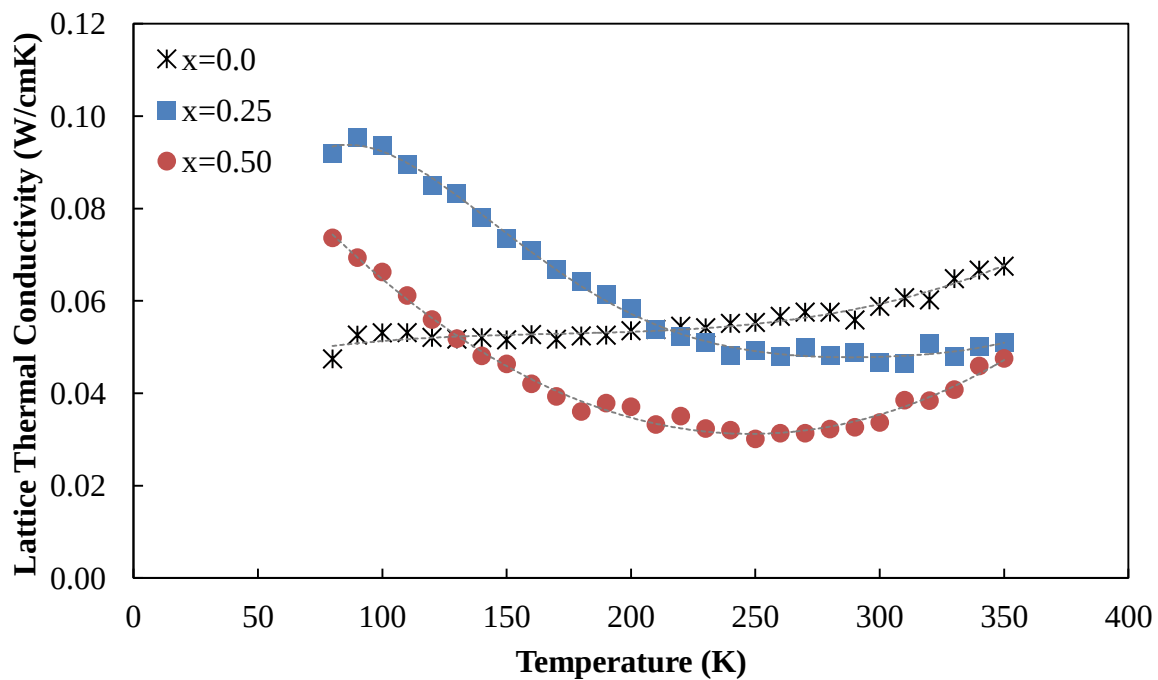


Figure 4-19: Lattice thermal conductivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25$, and 0.50 .

200K for the $x=0.50$ and 0.25 samples respectively, as can be seen in Figure 4-19. Unfortunately, the resistivity of these Er substituted samples is so rapidly reduced that the electronic component of the thermal conductivity is quite large and overwhelms any reduction of thermal conductivity from the lattice component. The total thermal conductivity is increased for all Er concentrations and is shown in Figure 4-20.

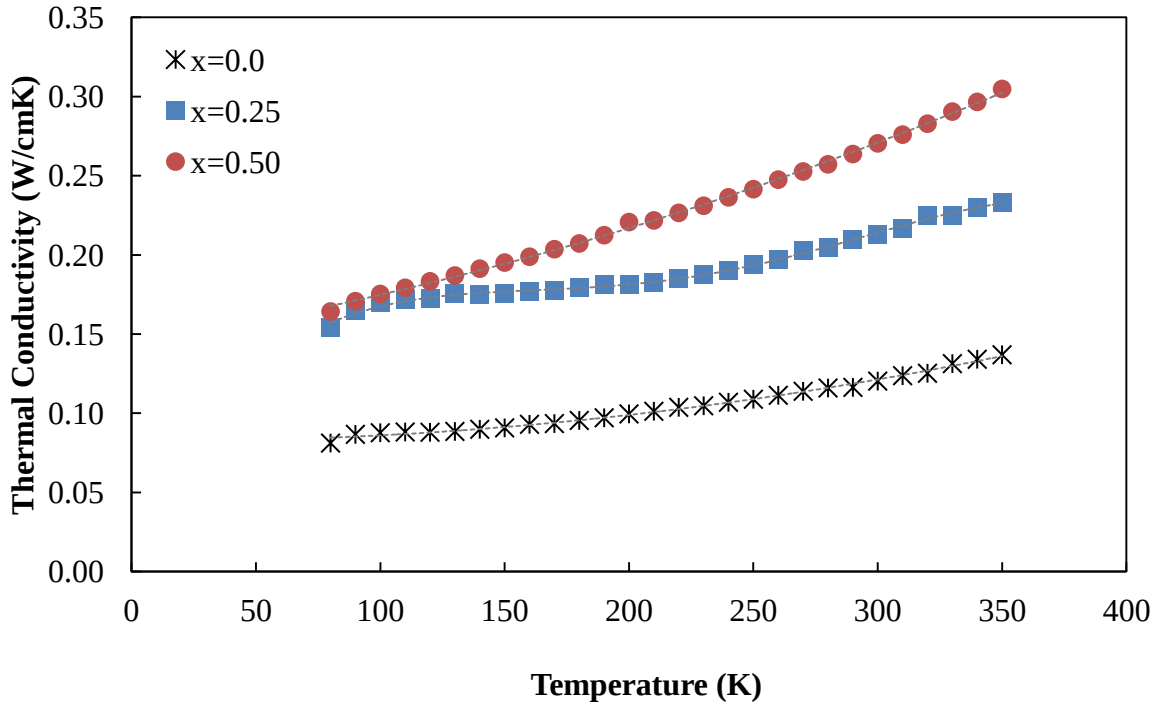


Figure 4-20: Total thermal conductivity from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25$, and 0.50 .

Combining the strongly enhanced power factor with the increased thermal conductivity results in an enhancement in the zT value for the Er $x = 0.25$ sample. The thermal conductivity of the $x = 0.50$ sample is too large to achieve an increase in the zT despite the doubled power factor, as can be seen in Figure 4-21. While higher Er concentration samples are not reported here, the trends indicate that each of the thermoelectric properties would become metallic, thus reducing power factor while increasing thermal conductivity. Therefore there is no reason to expect that

there would be any enhancement in the zT for high concentration Er samples.

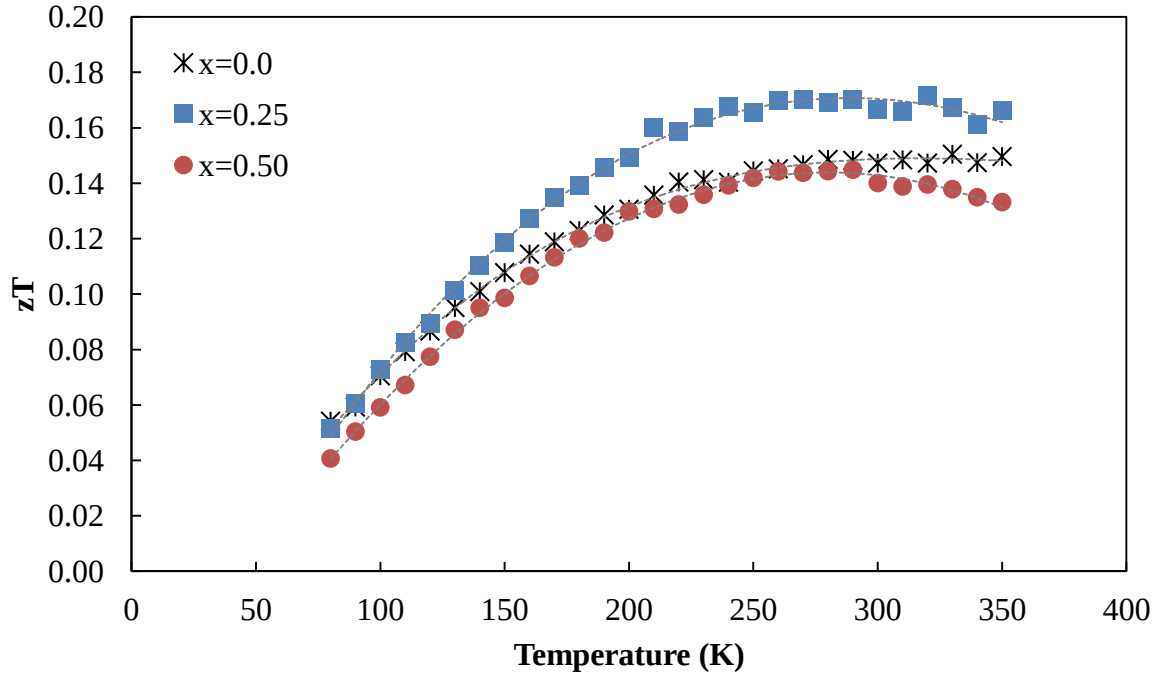


Figure 4-21: The dimensionless figure of merit from 80K to 350K for the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25$, and 0.50

4.5 $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$

A third element, lutetium, was also used to create a solid solution with YbAl_3 . This solid solution was synthesized with the goal of reducing the lattice thermal conductivity without having significant affects on the electronic properties. Similarly to the previous solid solutions, LuAl_3 and YbAl_3 are isostructural compounds, thus forming a full solid solution. Previous researchers collected magnetic data on $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ single crystals in order to better understand and analyze the theoretical explanations of the YbAl_3 intermediate valence system [74]. While this study shows that a full solid solution is possible for this system, no bulk polycrystalline samples have been made and no thermoelectric properties were measured.

4.5.1 Synthesis

Similarly to the Yb-Al phase diagram, the Lu-Al phase diagram [86] shown in Figure 4-22 demonstrates a peritectic reaction, although the transition temperatures have not been accurately determined in this case. In order to achieve a phase pure sample an Al-rich environment was again utilized to synthesize the phase pure LuAl_3 , starting with the nominal LuAl_5 composition. By arc-melting followed by etching, pure LuAl_3 was synthesized and subsequently ball milled together with YbAl_3 powder to create $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0 .

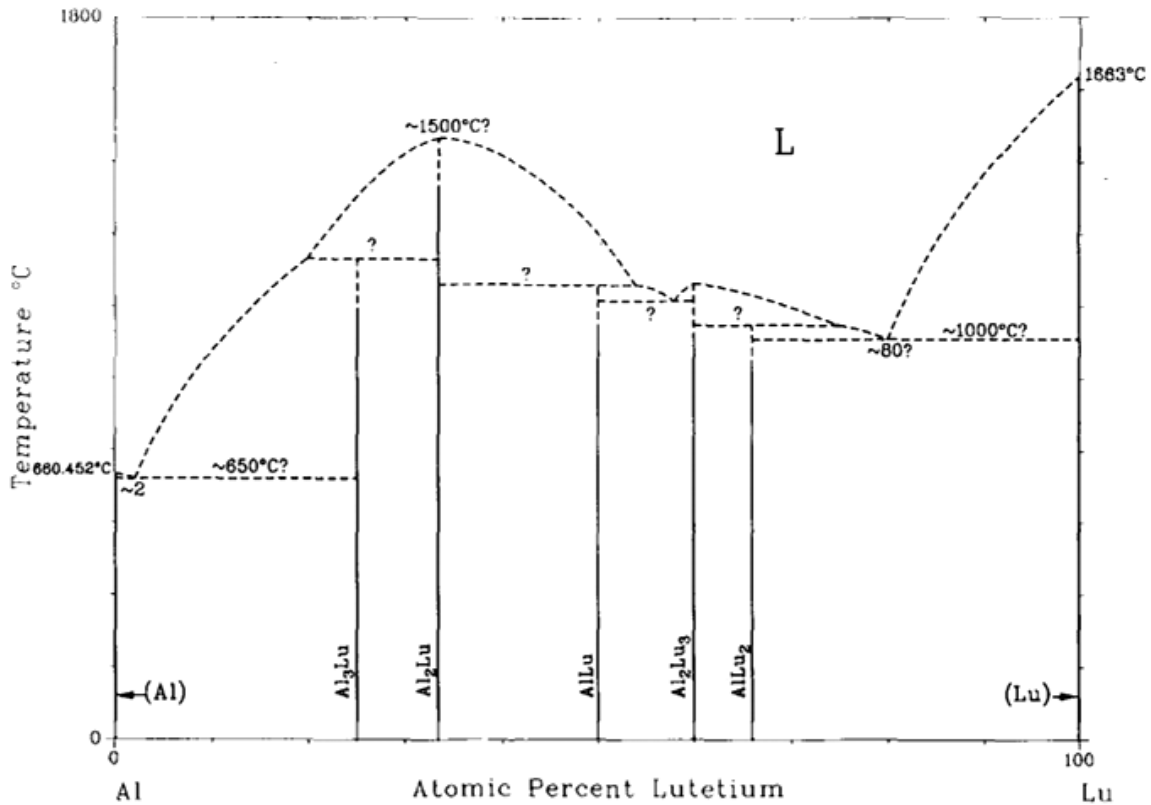


Figure 4-22: The Lutetium-Aluminum binary phase diagram by H. Okamoto [86].

4.5.2 Characterization

LuAl_3 forms in the L1_2 crystal structure as confirmed by the XRD pattern. The XRD patterns, shown in Figure 4-23, also revealed the same small oxide impurity peaks as seen in the other YbAl_3 solid solutions but are not as overwhelming as those seen in the $\text{Yb}_{1-x}\text{Er}_x\text{Al}_3$ solid solution. No shift is observed in the characteristic peaks because the change in the lattice parameter is minimal due to the similarity in size of Yb and La.

The SEM micrograph, shown in Figure 4-24, shows grain sizes on the order of several microns. This micrograph is very similar to those of the YbAl_3 and ScAl_3 other base compounds.

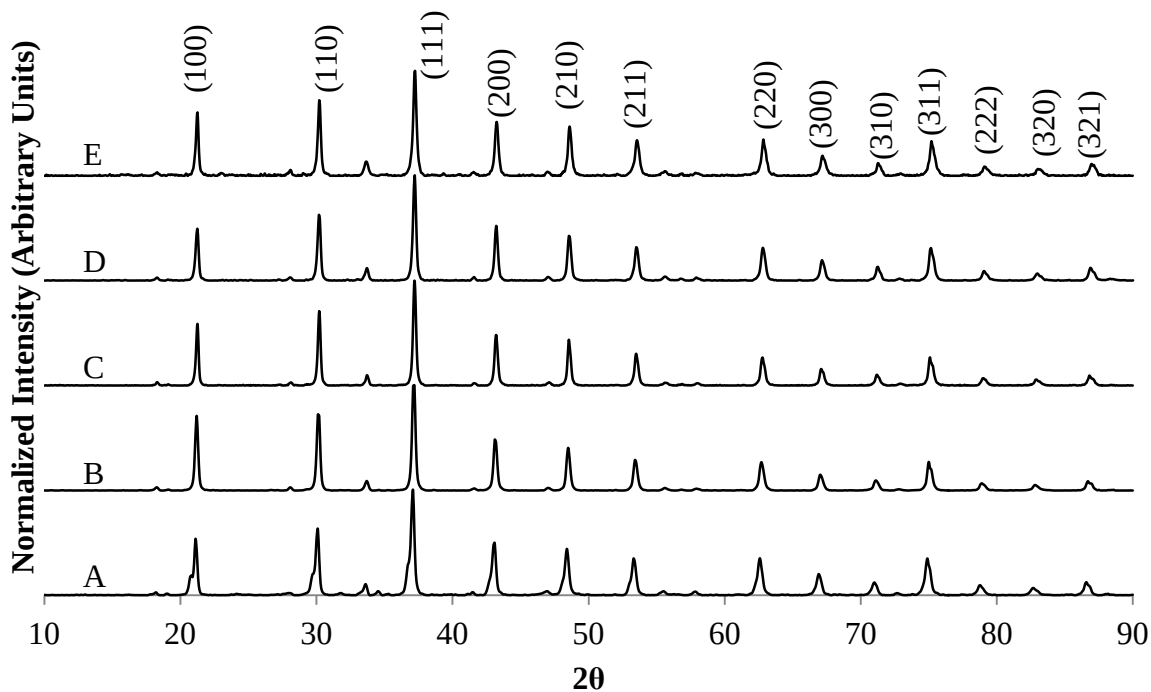


Figure 4-23: XRD pattern of the $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ solid solution at room temperature where A) $x = 0.0$, B) $x = 0.25$, C) $x = 0.50$, D) $x = 0.75$, and E) $x = 1.0$.

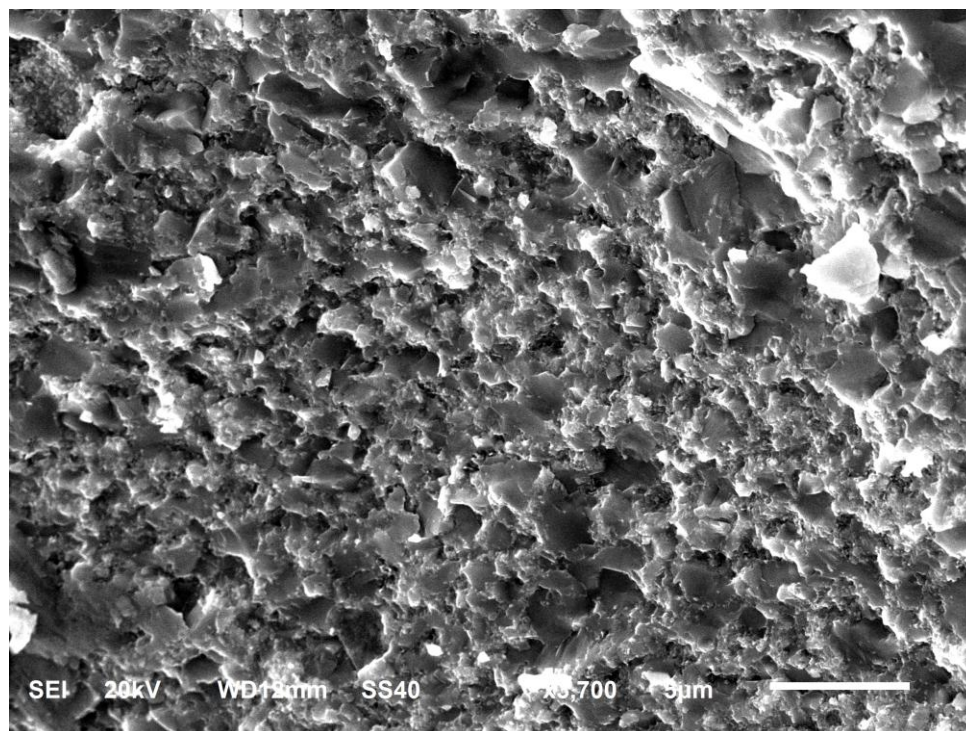


Figure 4-24: SEM images of fractured surfaces for LuAl_3 .

4.5.3 Transport Properties

Substituting even a small amount of Lu for Yb causes a dramatic decrease in the electrical resistivity. Similar to the Sc and Er solid solutions, at $x=1.0$, the resistivity (Figure 4-25) is as low as a very good metal. The magnitude of the Seebeck coefficient also decreases with increasing Lu content as can be seen in Figure 4-26. This decrease in Seebeck coefficient is not as rapid as that of the electrical resistivity, therefore there is an increase in the power factor for $x = 0.25$ and 0.50 across the entire temperature range as can be seen in Figure 4-27. This power factor for the Lu $x = 0.25$ sample is nearly double that of pure YbAl_3 , replicating the results achieved by the Er solid solution.

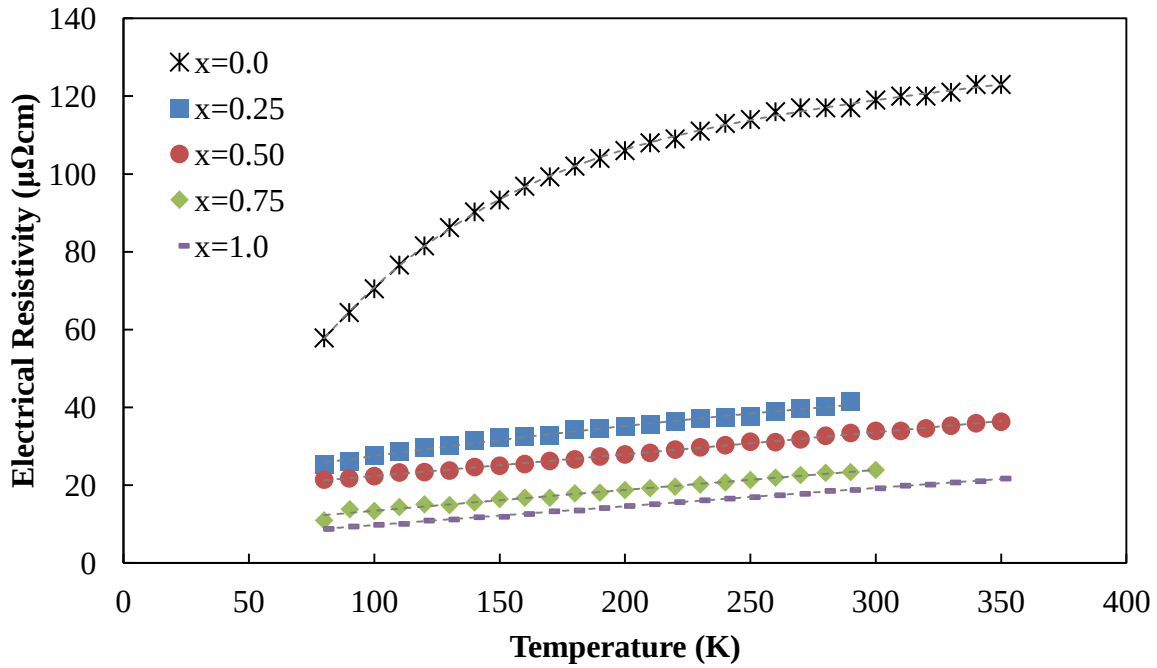


Figure 4-25: The electrical resistivity from 80K to (300K) 350K for $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0 .

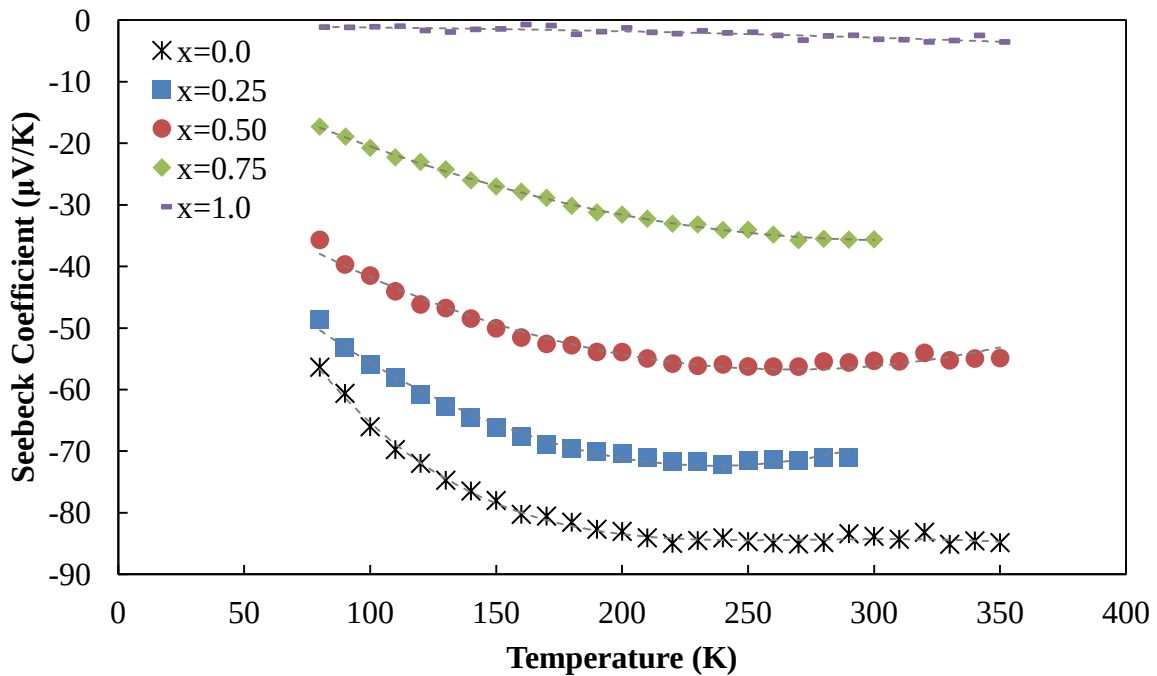


Figure 4-26: The Seebeck coefficient from 80K to (300) 350K for the $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0 .

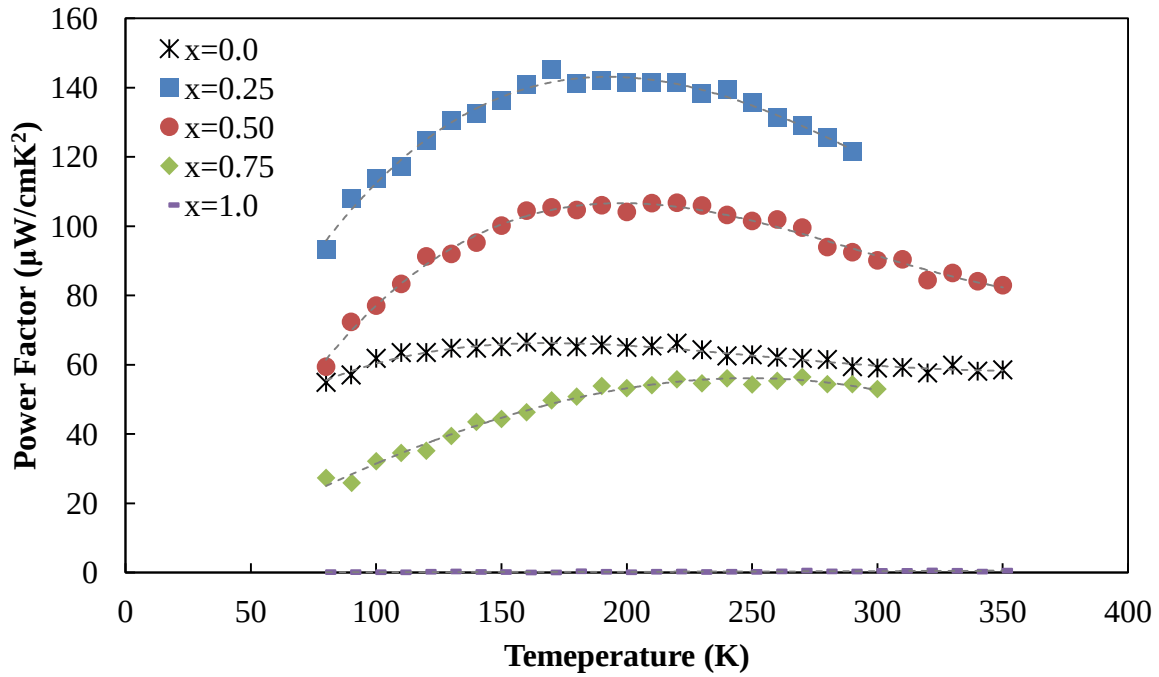


Figure 4-27: The power factor from 80K to (300K) 350K for the $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ solid solution where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0 .

While the reduction to the electrical resistivity helps to enhance the power factor, it also causes an increase in the electronic component of the thermal conductivity. The Lu substitution, does however induce some phonon scattering and reduces the lattice component of the thermal conductivity particularly at higher temperature, as shown in Figure 4-28. With the reduction in lattice thermal conductivity offsetting only some of the increase in the thermal conductivity from the electronic contribution, the total thermal conductivity, plotted in Figure 4-29, is increased for all concentrations of Lu.

Fortunately, the increase in the power factor is large enough to overcome the increase in the thermal conductivity for the Lu $x=0.25$ sample and the zT value is increased across the entire temperature range. As seen in Figure 4-30, the increase in the thermal conductivity for all other concentrations of Lu is too large and the zT is reduced.

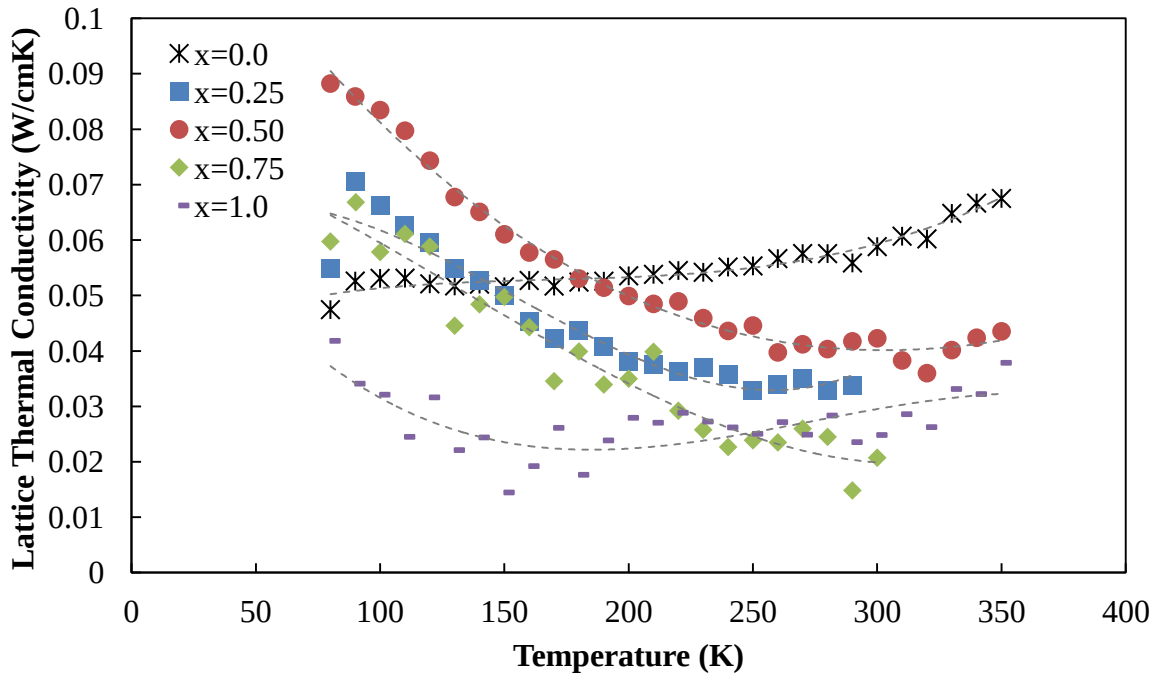


Figure 4-28: The lattice thermal conductivity from 80K to (300K) 350K for Yb_{1-x}Lu_xAl₃ where x = 0.0, 0.25, 0.50, 0.75, and 1.0.

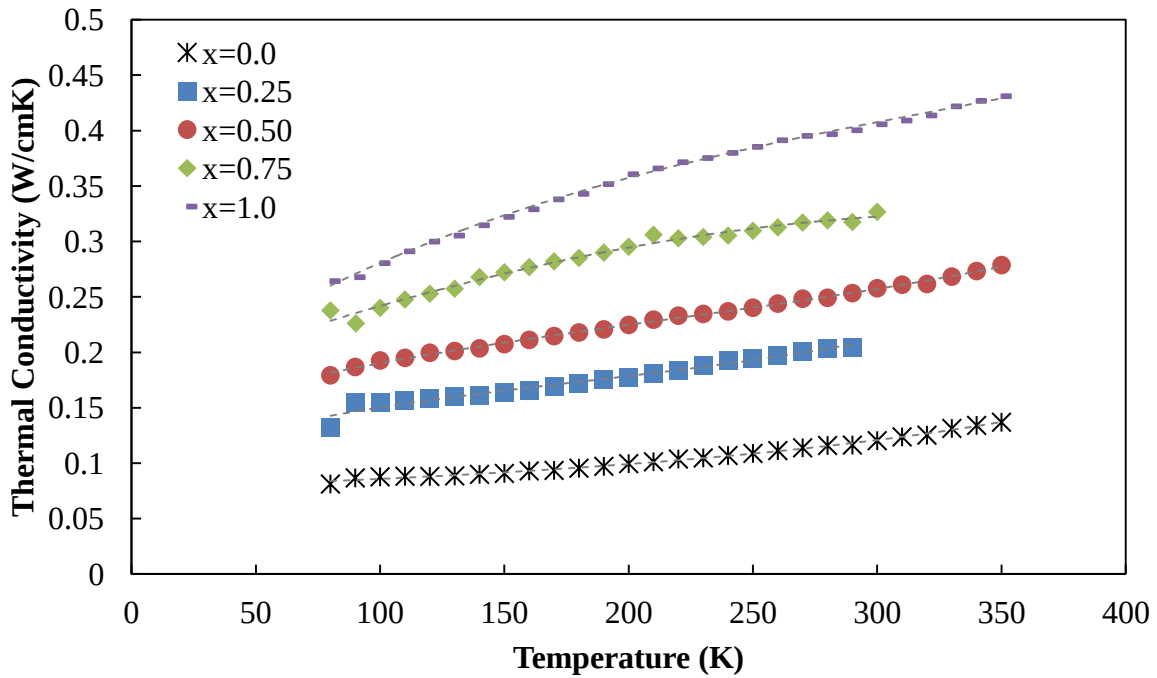


Figure 4-29: The total thermal conductivity from 80K to (300K) 350K for the Yb_{1-x}Lu_xAl₃ solid solution where x = 0.0, 0.25, 0.50, 0.75, and 1.0.

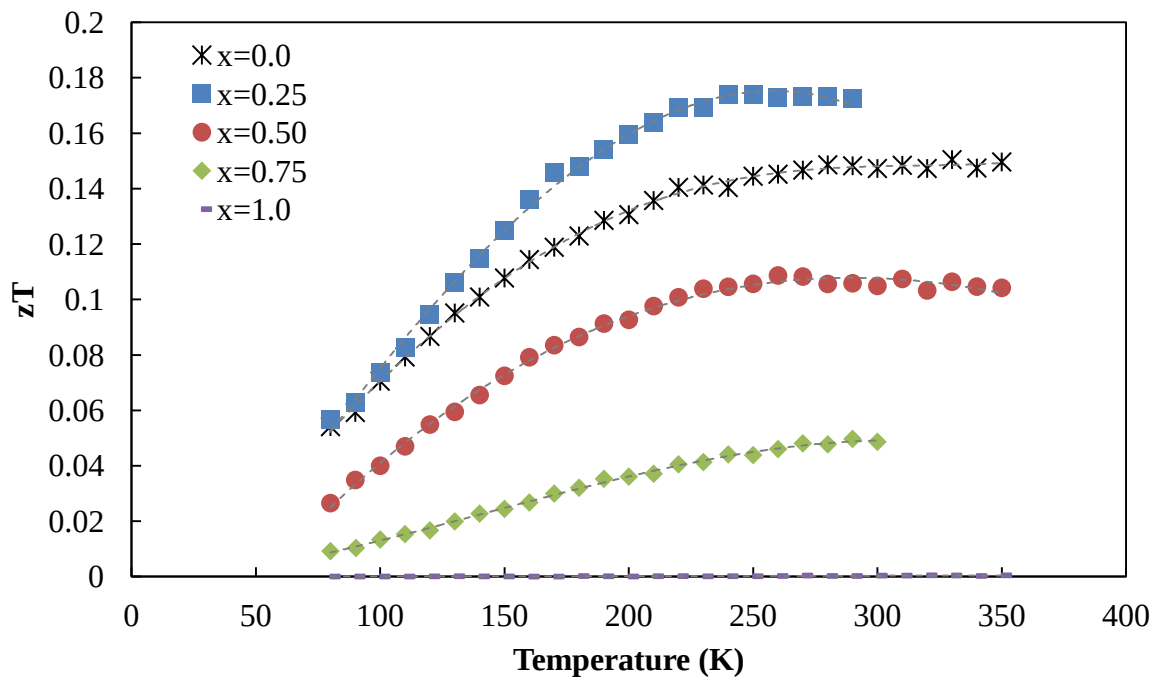


Figure 4-30: The thermoelectric dimensionless figure of merit from 80K to (300K) 350K for $\text{Yb}_{1-x}\text{Lu}_x\text{Al}_3$ where $x = 0.0, 0.25, 0.50, 0.75$, and 1.0 .

4.6 Summary

This chapter has demonstrated a new synthesis method for tri-aluminide compounds that allows for the fabrication of large polycrystals of YbAl_3 and related compounds for thermoelectric measurements. This work has investigated how substitution on the Yb site of YbAl_3 affects the thermoelectric transport properties. Generally speaking, isoelectronic substitutions create alloys that are more metallic in electrical and thermal conductivity, while the Seebeck coefficient is minimally altered for very small substitutional concentrations. This small reduction in the Seebeck coefficient and large drop in the electrical resistivity is a general characteristic of this family of compounds and results in enhanced power factor values. The already large power factor achieved by YbAl_3 is doubled for the Er and Lu solid solutions where $x=0.25$ and

enhanced across the entire temperature range for each solid solution where $x \leq 0.50$. However, the reduced electrical resistivity also caused a large increase in the electronic contribution to the total thermal conductivity, which could not be completely compensated for by the reduction in the lattice thermal conductivity. While Sc substitution created the largest reduction in lattice thermal conductivity, the large total thermal conductivity is still the limiting factor in these compositions and must be further reduced in order to achieve additional improvement in the zT . The thermoelectric figure of merit is enhanced for $x = 0.25$ samples in each of the solid solutions, while the $x \geq 0.50$ samples are limited by the increased thermal conductivity. ZT values between 0.18 and 0.20 were achieved for compositions with $x = 0.25$ for each alloy of Sc, Er and Lu with Yb, which is an enhancement of approximately 25% when compared to the pure YbAl_3 polycrystalline sample.

Creating solid solutions between YbAl_3 and $(\text{Sc, Er, Lu})\text{Al}_3$ resulted in enhance zT values, however there is still further optimization that must be done in order to achieve a material that is adequate for low-temperature thermoelectric applications. Reduction of the thermal conductivity of these materials would be necessary to achieve a material with a zT feasible for applications. Two potential approaches for further study are reducing grain size and substituting on the Al site. While this work used high energy ball milling to reduce particle size, neither this process nor the pressing procedure were optimized to maintain small grain sizes in the final densified puck. By reducing the final grain size, it is possible to further scatter phonons without disrupting the electronic transport properties. Isoelectronic substitution on the Al site would create additional scattering sites within the lattice, providing a means to further reduce the lattice thermal conductivity. As mentioned in the introduction of this chapter, attempts were made to synthesize YbIn_3 and YbSn_3 compounds for substitution; however, phase-pure samples were not

achieved. There is theoretical evidence that these phases should form and create a full solid solution with YbAl_3 ; however, it appears that they may require single crystal synthesis, which is beyond the scope of this work. Substitution on the Al site may also have a dissimilar affect on the electronic properties than the Yb site substitution, potentially creating a means to tailor the electrical resistivity and limit the electronic contribution to the thermal conductivity.

The thermoelectric properties of the well-known intermediate valence compound YbAl_3 were improved by forming isoelectronic solid solutions with ScAl_3 , ErAl_3 , and LuAl_3 . This work demonstrated that not only is this compound promising for low-temperature thermoelectrics, but other Yb-based compounds may also be enhanced by simple solid solution alloying. The following chapters will further investigate Yb-based compounds and the effects of solid solution alloying on the thermoelectric properties due to changes in the Yb valence via magnetic investigations.

Chapter 5 YbAl₂-Based Solid Solutions

5.1 Introduction

YbAl₂ is an intermediate valence compound that has been studied for the effects of external and internal pressures on the average Yb valence [45,46,49,50,53]. The valence of the Yb atom, which is approximately 2.2 at room temperature for the base YbAl₂ composition, can be easily affected by chemical substitution. By substituting a smaller atom on the Yb site, the size of the unit cell can be reduced and the Yb atom is forced into a higher valence state with a smaller radius. The atomic structure of this compound is the C15 cubic Laves MgCu₂ structure [45,50,79,87,88] as shown in Figure 5-1. This structure is more complex than the YbAl₃ structure, thus it is expected to have an intrinsically lower lattice thermal conductivity.

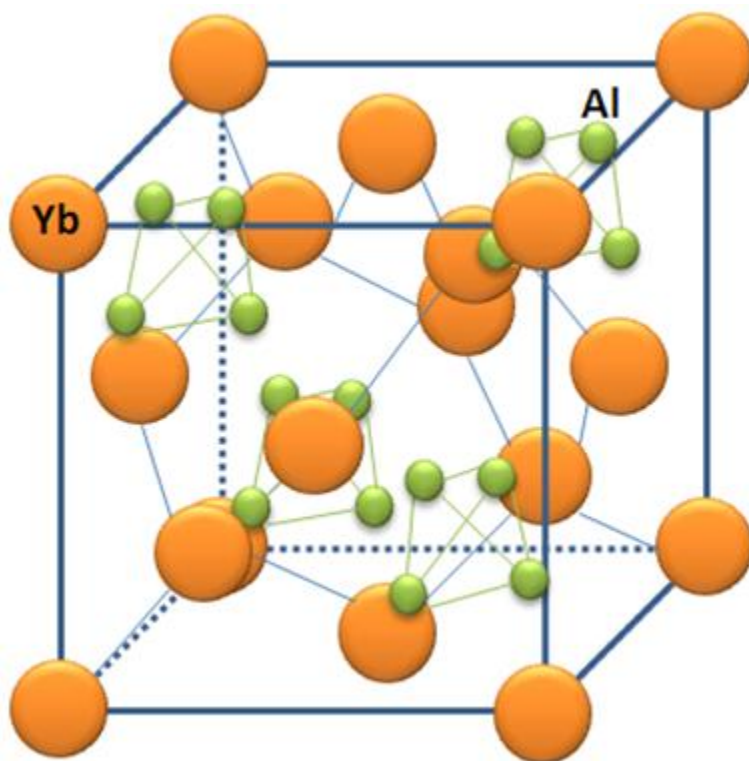


Figure 5-1: Unit cell diagram of YbAl₂.

While the relationship between Yb valence and magnetic properties has been heavily investigated, no research has been done on the effect of these valence changes to the Seebeck coefficient and other thermoelectric properties. YbAl_2 itself is a very poor thermoelectric material because of its nearly metallic Seebeck coefficient. However, if the average Yb valence and the Seebeck coefficient are directly connected as hypothesized, it may be possible to increase this Seebeck coefficient through chemical pressure. This work investigates the changes in thermoelectric properties as Sc is substituted for Yb in YbAl_2 and the relationship between these changes and the average Yb valence as calculated via magnetic properties. The results reported here have been previously published in the Journal of Applied Physics [89].

5.2 $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$

The solid solution between YbAl_2 and ScAl_2 is ideal because there is not only a large mass mismatch that can cause a reduction in the lattice component of the thermal conductivity, but Sc and Yb also have a large size mismatch which can be used to tailor the average Yb valence [49]. It is well understood that intermediate valence systems show changes in the Seebeck coefficient depending on the magnetic state of the f-ions, or in this case the Yb atoms [33,34]. Substitution on this site causes variation in the magnetic susceptibility through compression or expansion of the unit cell, resulting in a change in the average Yb valence and the Seebeck coefficient. There is also a large mass mismatch between the Sc and Yb atoms, as previously discussed in Section 4.3, which have the potential to induce a large reduction in the lattice thermal conductivity. Thus, chemically substituting Sc for Yb could be used to both optimize the Seebeck coefficient as well as reduce the lattice thermal conductivity through phonon scattering. Previous research has investigated the average Yb valence [49] and the magnetic susceptibility [57] of these solid

solutions, however these properties have not been experimentally compared to the Seebeck coefficient and other thermoelectric properties.

5.2.1 Synthesis

The high vapor pressure of Yb makes synthesizing pure YbAl_2 quite difficult, as maintaining the stoichiometric amount of Yb is nearly impossible. Just as excess Al was used to make YbAl_3 , in this case excess Yb was necessary to force the molten material to crystallize in the YbAl_2 phase due to the volatility of pure Yb metal. The nominal composition YbAl was arc melted only enough to combine the two pure materials and begin the alloying process. The sample was then subjected to a heat treatment that allowed the YbAl_2 phase to homogenize while the excess Yb vaporized. This was done by sealing the sample in a tube as described in Section 3.1.2, and heating it to 980°C at a rate of $0.3^\circ\text{C}/\text{min}$ and then holding at that temperature for 24 hours. The tube was then quenched in a room temperature water bath. This process resulted in a high quality sample that could be easily pulverized and used to create the solid solution with ScAl_2 . The ScAl_2 binary compound was synthesized via direct arc melting of the stoichiometric quantities of Sc and Al metals. The ScAl_2 sample was then pulverized and mixed with the YbAl_2 binary compound in stoichiometric quantities. The binary compounds were ball milled together for 20 minutes before they were sieved through a 60-mesh screen and densified. PECS was performed for 30 minutes under 60 MPa of pressure at 800°C . This PECS procedure resulted in densities of at least 95% for all compositions with the exception of pure YbAl_2 , which was not synthesized. This sample was ignored as there is literature data on the thermoelectric properties, none of which are particularly interesting [90,91]. The values given in the literature [90] are however used for the following discussions in order to provide a basis for comparison. Large

concentrations of Sc gave the most interesting thermoelectric results, thus $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ samples with concentrations of $x = 0.40, 0.60, 0.65, 0.70, 0.80, 0.85, 0.90, 0.95$, and 1.0 were formed.

5.2.2 Characterization

The phase purity of the samples was confirmed at each step in the process as can be seen in Figure 5-2, which shows the step-by-step XRD patterns of the YbAl_2 synthesis process. In these patterns, excess Yb peaks are clearly visible after the arc melting process but then disappear after the heat treatment process leaving only the desired YbAl_2 phase. The peaks are indexed according to the Miller indices observed via Görlach et. al [88]. The XRD patterns for the densified samples of the solid solutions are shown in Figure 5-3. A clear shift in the peaks indicate that the unit cell is shrinking as Sc concentration is increased, which is expressed more clearly in terms of the unit cell volume in Figure 5-4 as a function of Sc concentration. The values for the unit cell volume measured in this work match quite well with the data in the

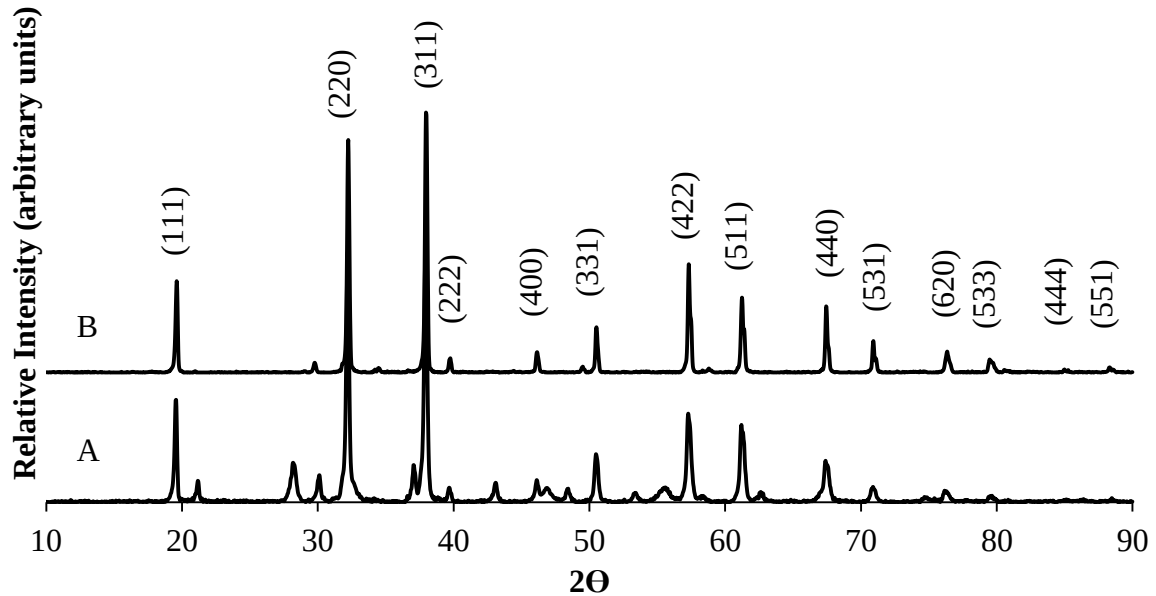


Figure 5-2: The XRD patterns at room temperature following the each of the steps in synthesizing YbAl_2 . A) after arc melting nominal YbAl where unlabeled peaks indicate a pure Yb phase, and B) pure YbAl_2 phase after 24 hour heat treatment.

literature [57] which are represented by the filled circles.

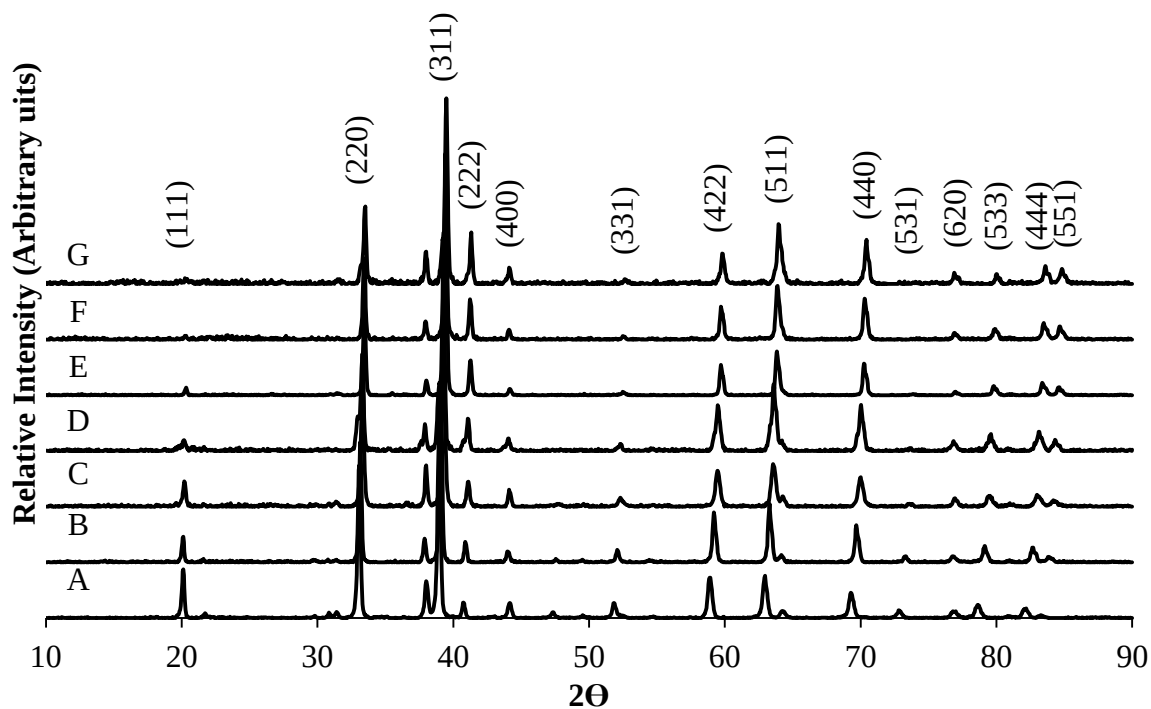


Figure 5-3: The XRD patterns for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where A) $x = 0.60$, B) $x = 0.70$, C) $x = 0.80$, D) $x = 0.85$, E) $x = 0.90$, F) $x = 0.95$, and G) $x = 1.0$.

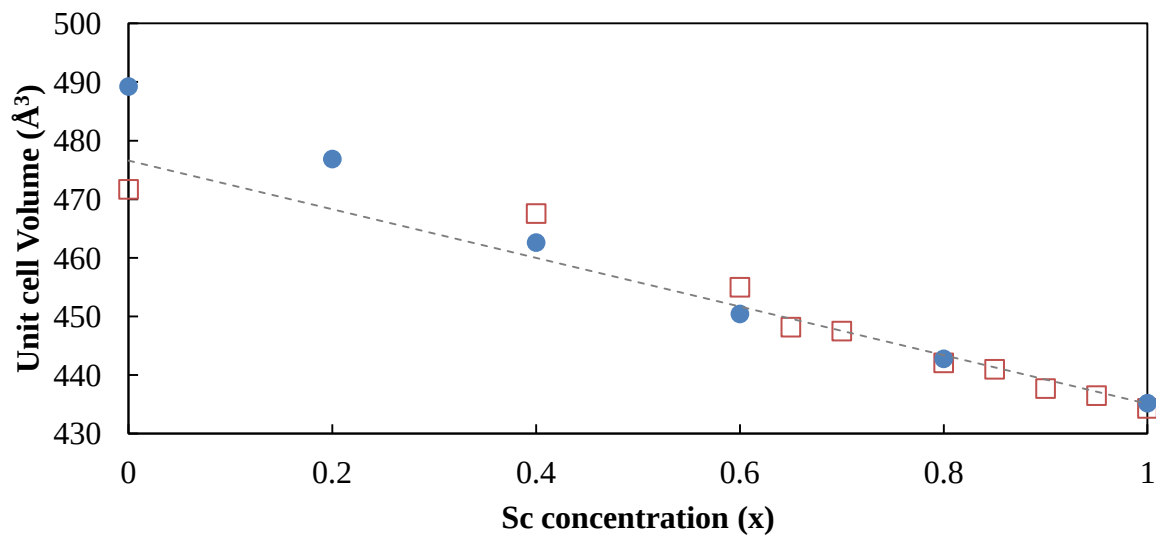
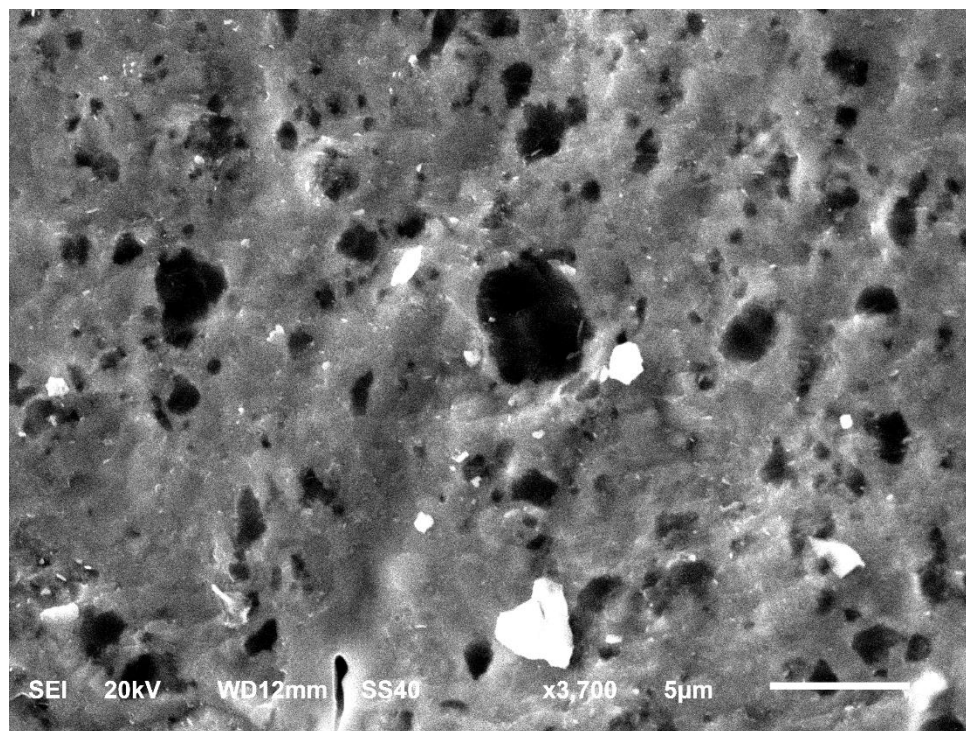


Figure 5-4: The unit cell volume as a function of Sc concentration at room temperature for $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ where $x = 0.0 \leq x \leq 1.0$. Closed circles are data from literature [57].

A



B

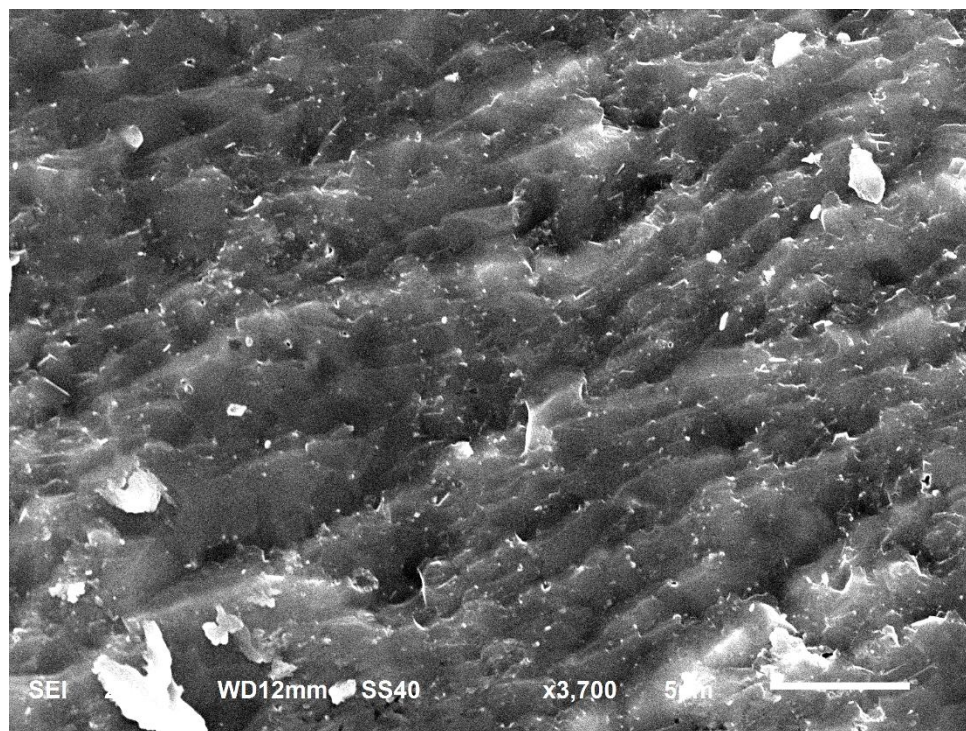


Figure 5-5: SEM images of fractured surfaces for A) $\text{Yb}_{0.60}\text{Sc}_{0.40}\text{Al}_2$ and B) ScAl_2 .

The microstructures of the $x=0.40$ and $x=1.0$ samples were examined using SEM. These images are shown in Figure 5-5. Grains on the order of several microns are observed, similarly to those previously discussed in the tri-aluminide series. Small impurity phases were qualitatively identified by EDS as a $\text{Yb}_3\text{Al}_5\text{O}_{12}$ impurity phase. This phase is assumed to be rather insignificant towards the transport properties; however, it is taken into account later when examining the magnetic properties.

5.2.3 Transport Properties

The thermoelectric properties were measured on each of the samples in the solid solution from 80K to 350K. Several of the samples showed interesting trends at low temperatures and thus were measured by collaborators at Ohio State University from 2K to 300K. Literature data [90] was used for the $x=0$ sample for comparison to the samples measured in this study.

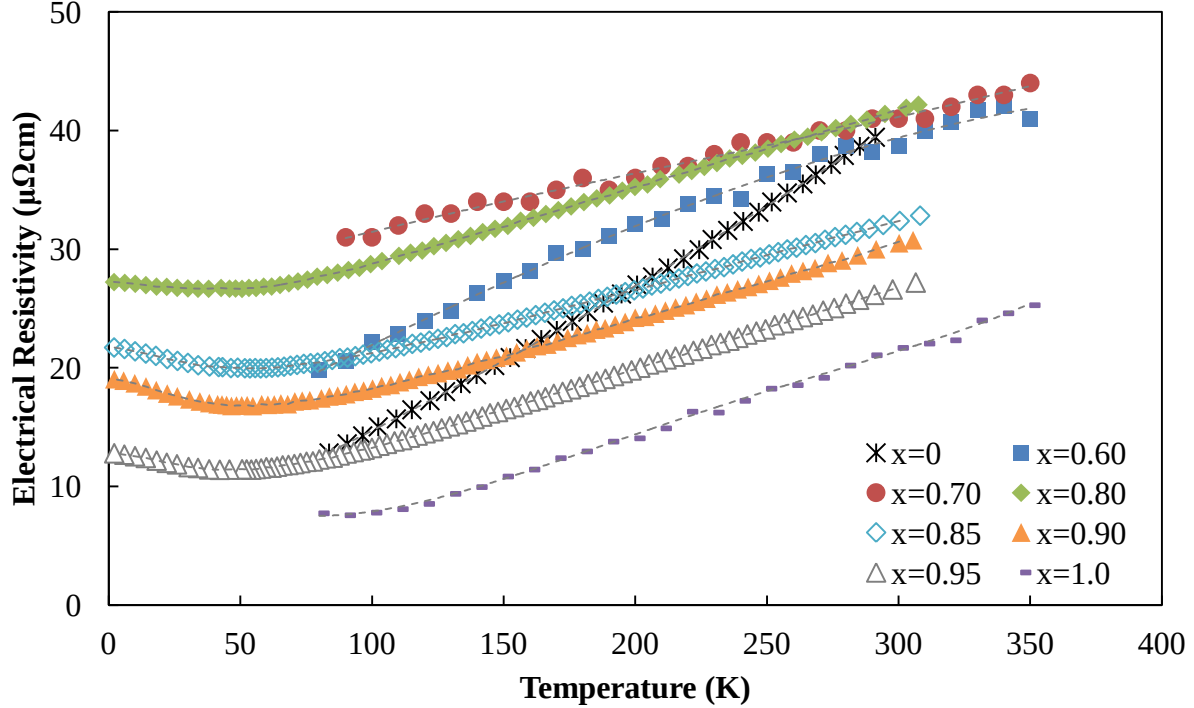


Figure 5-6: The electrical resistivity from 2K (80K) to 300K (350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0$ [93], 0.60, 0.70, 0.80, 0.85, 0.90, 0.95, and 1.0.

The electrical resistivity has a non-zero minimum for each of the samples measured at low temperatures shown in Figure 5-6. This trend is reminiscent of a Kondo-like behavior, but this detail is not explored further here. Above 100K the electrical resistivity follows an increasing linear trend with similar slopes for each of the compositions, with the exception of $x = 0$. The electrical resistivity increases with increasing Sc content up to $x = 0.80$, before it reaches a maximum and starts decreasing. The pure ScAl_2 sample has the lowest electrical resistivity of the solid solution, similar to the metallic ScAl_3 compound in the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_3$ solid solution.

The Seebeck coefficient also shows very interesting trends at low temperature with high concentration of Sc. The Seebeck coefficient reaches its largest magnitude of about $50\mu\text{V/K}$ at approximately 40K when the Sc concentration is $x = 0.90$. The Seebeck coefficient plotted in

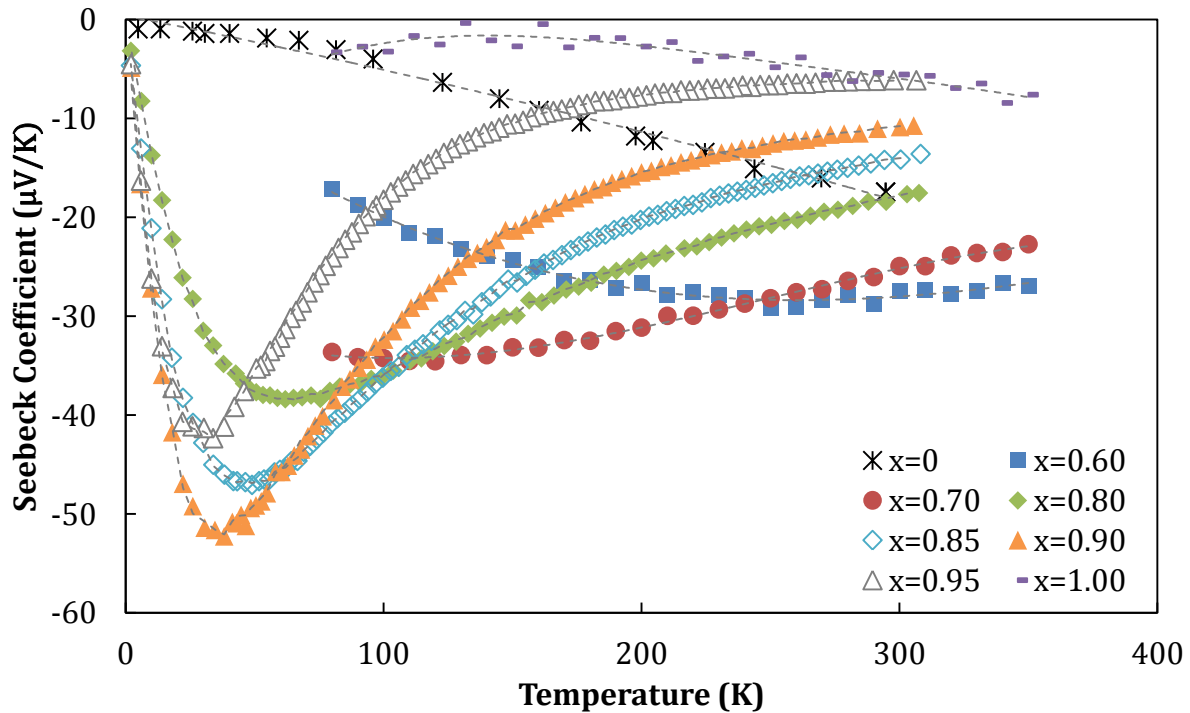


Figure 5-7: The Seebeck coefficient from 2K (80K) to 300K (350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0$ [93]. 0.60, 0.70, 0.80, 0.85, 0.90, 0.95, and 1.0

Figure 5-7 shows an increase in the magnitude as well as a shift towards lower temperatures with increasing Sc content, except for $x=0.95$, where the magnitude is reduced from the $x=0.90$

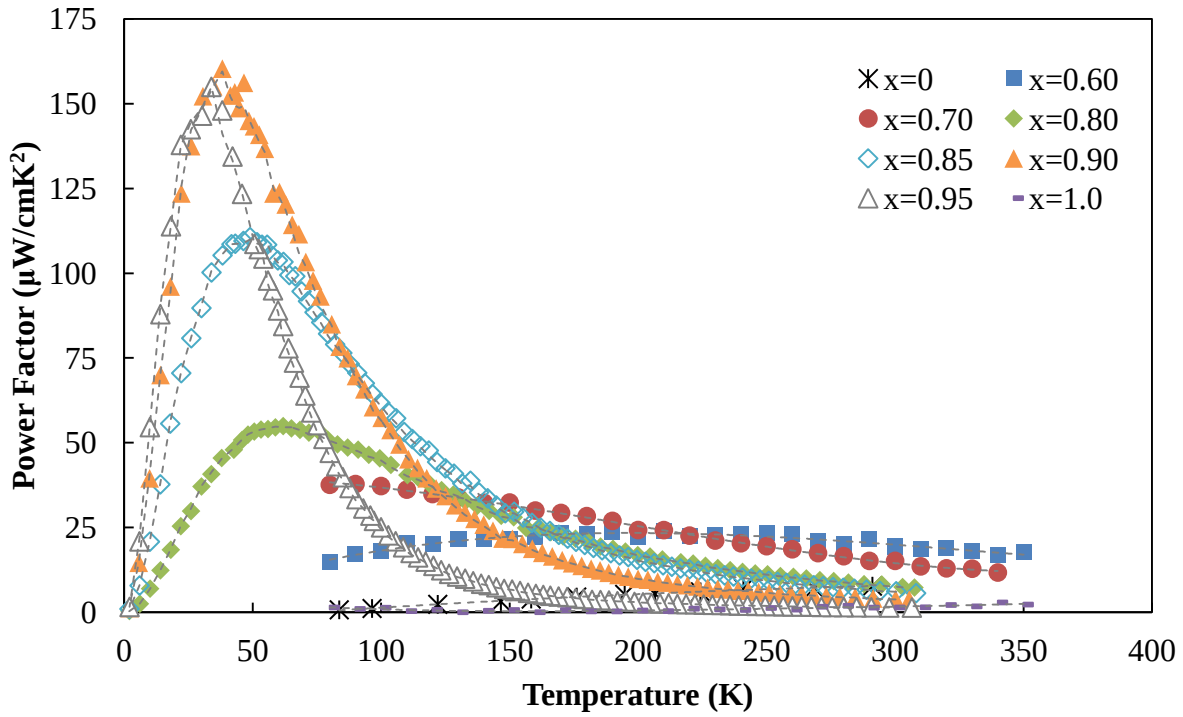


Figure 5-8: The power factor from 2K (80K) to 300K (350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0$ [93], 0.60, 0.70, 0.80, 0.85, 0.90, 0.95, and 1.0.

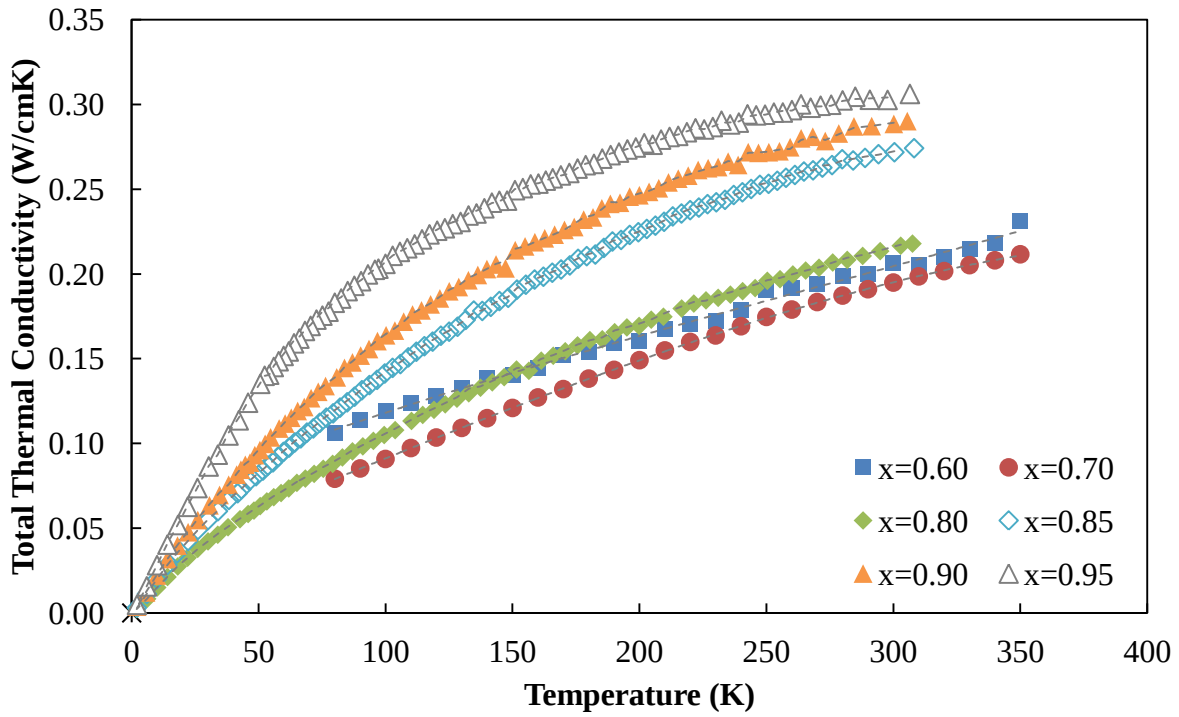


Figure 5-9: The total thermal conductivity from 2K (80K) to 300K (350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90$, and 0.95.

sample. The peaks in the Seebeck coefficient are large, especially in comparison to the literature values reported for YbAl_2 ; however, they are also very narrow. Combining the sharp peaks in the Seebeck coefficient with the decreased electrical resistivity, the power factor rises to enormous values within a very small temperature range, as shown in Figure 5-8. The power factor reaches a value near $160 \mu\text{W}/\text{cmK}^2$, which is even larger than that reported for the YbAl_3 solid solutions. This tremendous power factor at cryogenic temperatures (40K) is significant and the largest value achieved in this temperature range by a bulk thermoelectric material to date. The total thermal conductivities for all samples in the solid solution except, for $x=0$ and 1.0, are shown in Figure 5-9. The $x = 1.0$ sample is not shown here because its thermal conductivity is greater than $0.6 \text{ W}/\text{cmK}$, making the scale difficult to observe the differences in the lower Sc concentration samples, and there is no literature data on the thermal conductivity of the $x = 0$ sample. As expected, the total thermal conductivity of the sample increases as the Sc concentration increases and becomes more metallic due to the increasing electronic contribution. Unfortunately, further reduction of the lattice thermal conductivity is likely to have little to no effect on the total thermal conductivity as the electronic contribution makes up a significant portion of the total thermal conductivity and cannot be reduced without detrimental affects to the power factor

The dimensionless figure of merit for these compositions follows a similar trend to the power factor, with a very narrow peak at low temperatures. The zT , shown in Figure 5-10, clearly demonstrates that the Sc content can be used to tailor the temperature range that optimizes the zT . There is little difference between the thermal conductivities in the cryogenic temperature range, thus the zT peaks occur at the same temperatures as the power factor and Seebeck coefficient. Unfortunately, each of the compositions results in very sharp peaks in the zT , which is not ideal for applications. Despite the dramatic increase in the Seebeck coefficient and power

factor at low temperatures, the zT value is still quite low due to the electronic contribution to the thermal conductivity. Despite the low zT value, these compositions provide a clear demonstration that alloying is a promising method for increasing Seebeck coefficient, power factor, and zT in intermediate valence systems, and for controlling the temperature at which these parameters are optimized. In order to better understand the underlying properties causing these low temperature peaks, magnetic measurements were done to investigate the average Yb valence as a function of temperature and composition.

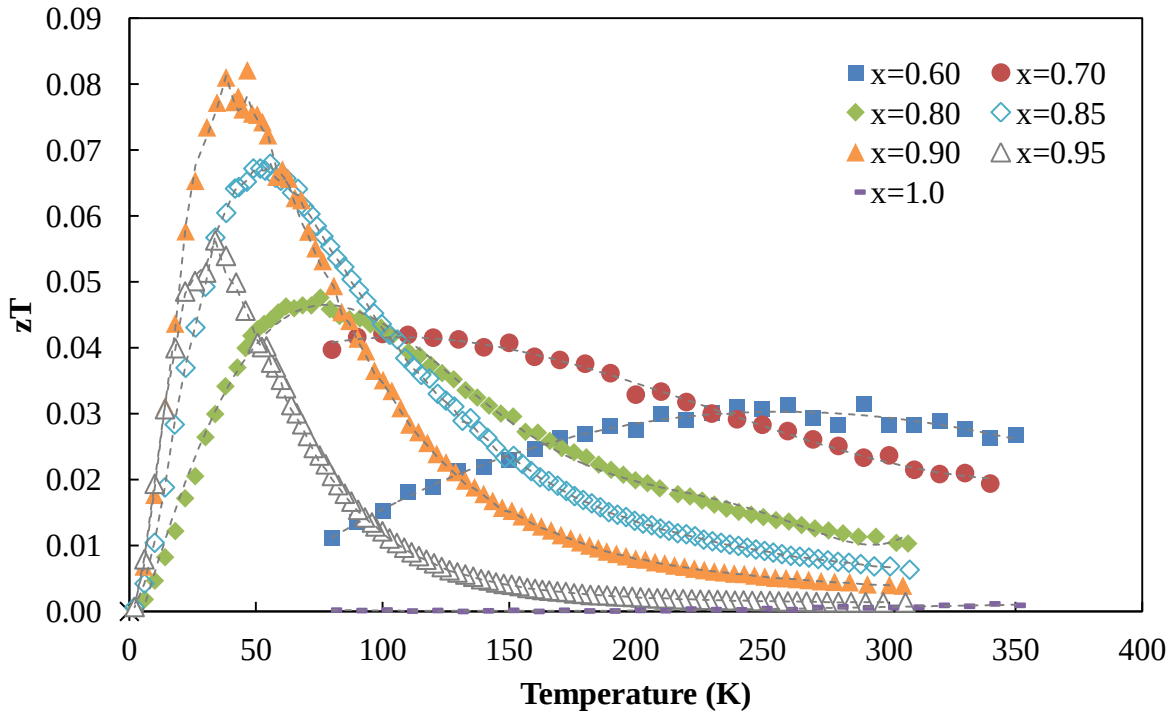


Figure 5-10: The zT from 2K(80K) to 300K(350K) for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90, 0.95$, and 1.0 .

5.2.4 Magnetic Properties

The magnetic moment was measured for each of the samples as a function of temperature. This data was collected as described in Section 3.3.2. Sales and Wholleben [40] previously proposed a model to fit the magnetic susceptibility of Yb-based intermediate valence compounds. This

model is known as the Interconfigurational Fluctuation (ICF) model, and is used here to extract the average Yb valence from the data. This model takes into account a temperature-dependent ratio of the Yb^{2+} and Yb^{3+} state, which have two independent energies ($E_{ex} = E_{3+} - E_{2+}$), angular momentums (J_3 or J_2), and effective magnetic moments as determined by Hund's rules (μ_3 or μ_2). By fitting two variables, the excitation energy (E_{ex}) and the spin fluctuation temperature (T_{sf}), to the temperature dependent magnetic susceptibility data, the average temperature-dependent Yb valence ($v(T)$) can be determined. For the ICF model, the susceptibility may be expressed as:

$$\chi = \frac{N(\mu_3^2 v(T) + \mu_2^2 (1 - v(T)))}{3k_B(T + T_{sf})} \quad v(T) = \frac{2J_3 + 1}{(2J_3 + 1) + (2J_2 + 1)e^{\left(\frac{-E_{ex}}{k_B(T + T_{sf})}\right)}}$$

which can be simplified for the Yb case. When Yb is in the $4f^{14}$ (divalent) state, $J_2=0$ and $\mu_2=0$, thus the model is reduced to a more simplified version using the values $J_3=7/2$ and $\mu_3=4.54 \mu_B$ for Yb in the $4f^{13}$ (trivalent) state as follows:

$$\chi = \frac{N(4.54\mu_B)^2 v(T)}{3k_B(T + T_{sf})} \quad v(T) = \frac{8}{8 + e^{\left(\frac{-E_{ex}}{k_B(T + T_{sf})}\right)}}$$

A correction was done to remove the background signal that was observed from the oxide impurity phase. The phase was identified as $\text{Yb}_3\text{Al}_5\text{O}_{12}$, which has a Yb valence of 3+. The large moment associated with the trivalent Yb ion creates a Curie tail at low temperature in the data. The Curie tail was fit between 2K and 10K according to $M=C/T$, where M is the magnetic moment, C is the Curie constant, and T is the temperature. The Curie constant is obtained from the slope of the M vs. $1/T$ curve. This impurity signal was then subtracted from the total moment and used to estimate the mass of the impurity phase. From the corrected moment and the corrected sample mass, the magnetic susceptibility was found per Yb atom, a quantity that could

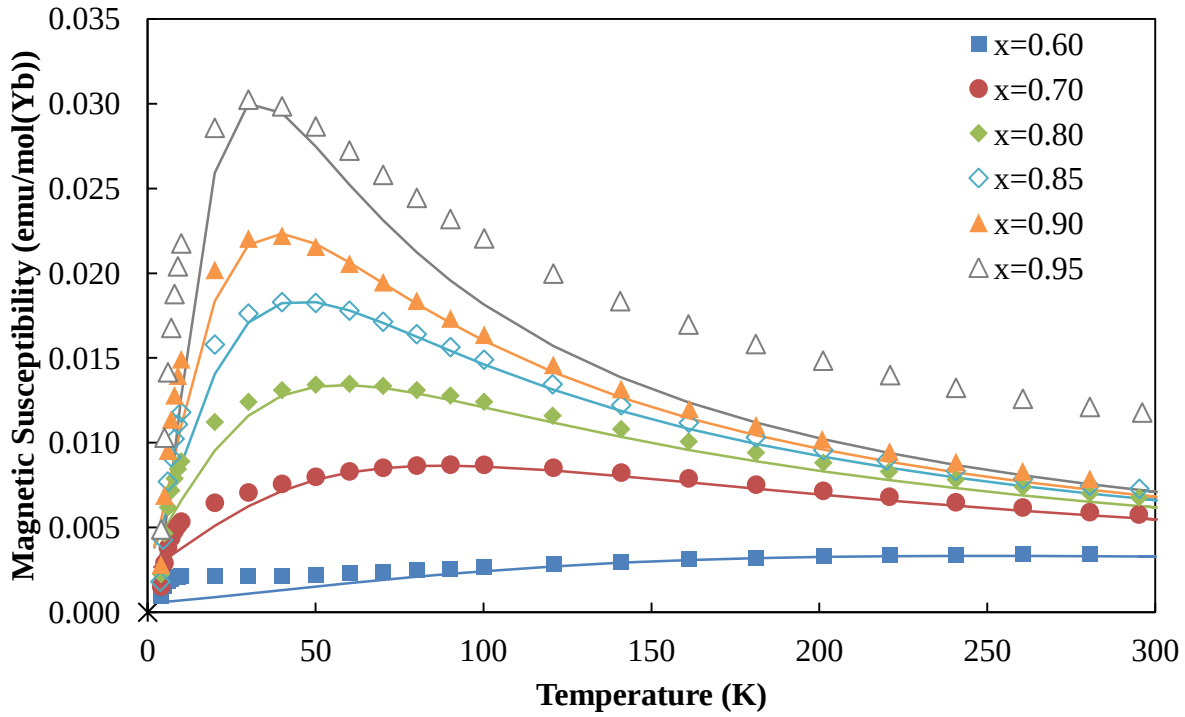


Figure 5-11: The corrected magnetic susceptibility data (points) and the corresponding ICF model fits (lines) from 2K to 300K for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90$, and 0.95

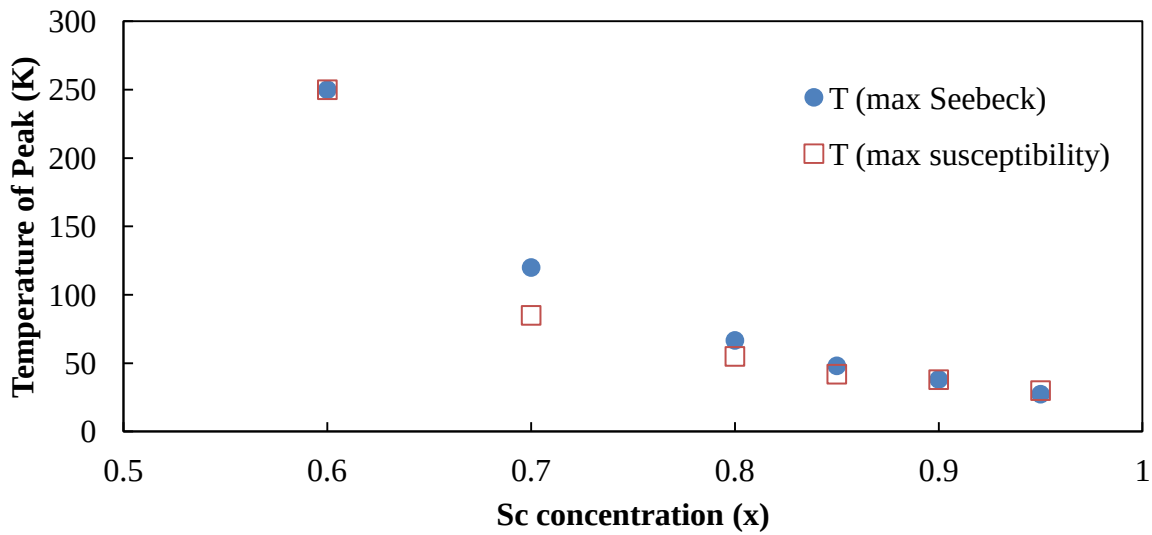


Figure 5-12: Comparison of the temperatures at which the magnitude of the Seebeck coefficient and the magnetic susceptibility are maximized as a function of Sc concentration.

be fit to the ICF model. The resulting curves were fit to the model by adjusting the two model parameters. The corrected data and their fits are shown in Figure 5-11.

The low temperature peaks in the magnetic susceptibility data are characteristic of intermediate valence systems. It can be seen that the temperatures at which these peaks occur correspond very closely with the temperatures at which the Seebeck coefficient peak for each composition; see Figure 5-12. This correlation provides strong evidence that the large Seebeck coefficient is driven and controlled by the valence fluctuations of the Yb atom. These interesting transport and magnetic data call for a direct investigation of the relationship between the average Yb valence and the Seebeck coefficient. Using the ICF model fits, the average Yb valence can be plotted as a function of temperature, as shown in Figure 5-13. The compression of the unit cell resulting from increased Sc content causes the Yb atom to have a less available space and thus the Yb atom spends more time in the trivalent state, which has fewer electrons ($4f^{13}$) and a smaller radius. The average Yb valence changes toward the trivalent state rather rapidly, and at

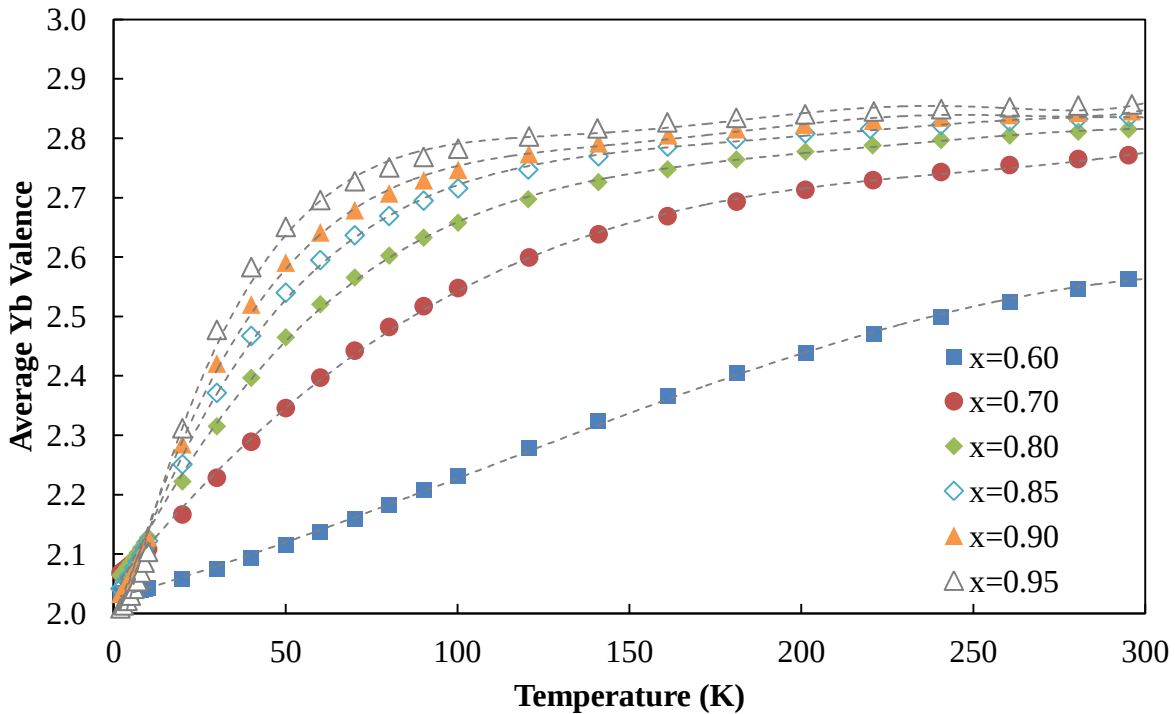


Figure 5-13: The average Yb valence as a function of temperature obtained from the ICF model for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90$, and 0.95 .

high Sc content the average Yb valence reaches 2.8 by 100K, as can be seen in Figure 5-13. The Seebeck coefficient can be plotted against this average Yb valence, which results in a revealing trend, shown in Figure 5-14.

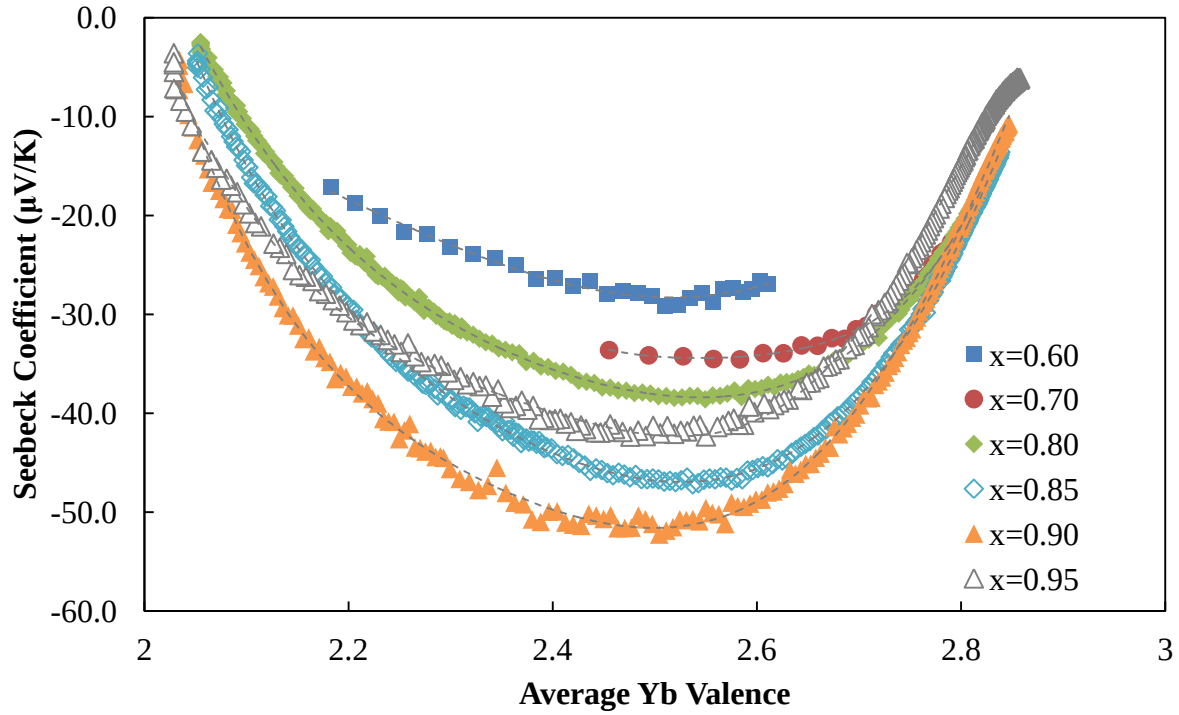


Figure 5-14: The Seebeck coefficient as a function of the average Yb valence for the $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution where $x = 0.60, 0.70, 0.80, 0.85, 0.90$, and 0.95 .

This figure demonstrates that the magnitude of the Seebeck coefficient is maximized, independent of composition, near an average Yb valence of 2.5. This result gives experimental evidence of the effects of Yb valence on the Seebeck coefficient as well as provides a specific goal for tailoring the Seebeck coefficient via tuning the average Yb valence in intermediate valence compositions. The narrow peak in the Seebeck coefficient can be understood by examining Figure 5-13 with respect to the relationship shown in Figure 5-14. If it holds true, as evidenced here, that the Seebeck coefficient peaks at the temperature where the average Yb valence curve passes near 2.5, it can be assumed that the Seebeck coefficient will only stay large

for temperatures where the average Yb valence remains near 2.5. The slopes of the average Yb valence curves are quite steep for large Sc content, and therefore the average Yb valence of each composition is only near 2.5 for small (or narrow) temperature ranges, consistent with the narrow peaks that are observed in the Seebeck coefficient. The temperature at which the Seebeck coefficient peaks also shifts towards lower temperatures as Sc is added to the system. This shift again can be explained by the average Yb valence curve, which increases more rapidly as the Sc content is increased, thus reducing the temperature at which an average Yb valence of 2.5 is achieved.

The relationship between the average Yb valence and Seebeck coefficient, as well as the shape of the average Yb valence vs. temperature curve demonstrated here, provide new insight into the desired characteristics of Yb-based intermediate valence compounds. One might speculate that the average Yb valence curve should have a magnitude near 2.5 and be flat across the entire temperature range to achieve a large Seebeck coefficient across the entire temperature range, meeting the needs of a good thermoelectric material for low-temperature applications.

5.3 Summary

The $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ solid solution does not show significant promise as a material for low temperature thermoelectric applications; however, this system does reveal important trends between the Seebeck coefficient and magnetic properties. YbAl_2 is an intermediate valence system with nearly metallic thermoelectric properties. Methods for altering the average Yb valence have been widely investigated in the literature, yet no work had been done to investigate the relationship between these valence changes and the Seebeck coefficient, which is known to be affected by the fluctuating Yb valence state. In this work, a new synthesis method for YbAl_2 was developed that suppressed the formation of the YbAl_3 phase resulting in a fairly high-purity

sample; further, bulk polycrystalline samples were large enough to carry out thermoelectric property measurements.

The thermoelectric properties of YbAl_2 were significantly enhanced by forming a solid solution with ScAl_2 . Large peaks in the Seebeck coefficient and intrinsically low electrical resistivity resulted in tremendous power factors, reaching a value of $160 \mu\text{W}/\text{cmK}^2$ near 50K. This large power factor is unfortunately paired with a large thermal conductivity resulting in a modest zT of 0.08 at 50K. The large peaks in the Seebeck coefficient are also quite narrow, further rendering these materials useless for applications.

The magnetic measurements on these samples showed trends similar to those shown in the literature, with a large peak in the magnetic susceptibility at low temperatures, typical of intermediate valence systems. These curves were fit by the ICF model and thus the average Yb valence was extracted for each sample as a function of temperature. This average valence was then directly compared to the temperature dependent Seebeck coefficient, yielding some of the most interesting and insightful results of this solid solution. The absolute value of the Seebeck coefficient, which is known to be strongly related to the intermediate valence state of Yb, is maximized in each sample where the average Yb valence is near 2.5, regardless of composition. A deeper understanding of the fundamental physics of this relationship would be very desirable, but is beyond the scope of this work.

$\text{YbAl}_2\text{-ScAl}_2$ is an ideal system for demonstrating the effects of chemical pressure on the average Yb valence and thus showing the relationship between the Yb valence and the Seebeck coefficient. While there is little potential for thermoelectric applications using this particular compound due to the dominance of the electronic contribution to the thermal conductivity, the

new understanding regarding the relationship between average Yb valence and Seebeck coefficient has provided a guide for enhancing other intermediate valence Yb-based compounds. Chemical pressure may be used to systematically study the thermoelectric properties of intermediate valence systems as a function of average Yb valence, and an average Yb valence near 2.5 is ideal for this and possibly other similar systems. This experimental evidence has offered new insight into low temperature intermediate valence compounds and provided a specific goal for tailoring other Yb-based compounds with potential as low-temperature thermoelectrics.

Chapter 6 YbCu₂Si₂-Based Solid Solutions

6.1 Introduction

YbCu₂Si₂ has been reported several times in the literature [54,55,92-95] as an intermediate valence system with a relatively large Seebeck coefficient at low temperatures. This compound is promising because there are several solid solutions that can be investigated to maximize the thermoelectric figure of merit. Solid solutions are used to alter the lattice parameter and thus the average Yb valence as well as reduce the lattice thermal conductivity via disruption of phonon propagation. The transport properties, particularly the Seebeck coefficient, can be compared to the average Yb valence. As shown in the last chapter, the work on the YbAl₂-ScAl₂ solid solution demonstrated a maximum in the magnitude of the Seebeck coefficient when the average Yb valence is near 2.5. YbCu₂Si₂-based alloys provide another system on which the versatility of this behavior can be tested. The first solid solution investigated here is YbCu₂Si₂-YbCu₂Ge₂. The unit cell volume should be increased as Ge is substituted for Si, as it has a larger atomic radius, and thus the average Yb valence should be reduced as it is allowed more space to assume the divalent state. The second solid solution reported here is YbCu₂Si₂-LaCu₂Si₂. Alloying with La may also create lattice expansion, as the La atom has a larger atomic radius than the Yb atom. YbCu₂Si₂ has an average Yb valence of approximately 2.75 at room temperature, and therefore expanding the unit cell should cause the average Yb valence to shift toward a more divalent state, ideally approaching the target average Yb valence of 2.5.

YbCu₂Si₂, and its isostructural compounds used for alloying, have a tetragonal unit cell of the ThCr₂Si₂-type crystal structure [44,47,48,92,96-99], shown in Figure 6-1. This structure has a smaller lattice thermal conductivity than the YbAl₃ and YbAl₂ compounds previously

investigated in this report because of a more complex phonon spectrum. This difference suggests that alloying may not have the same impact on reducing the lattice thermal conductivity as it has in the previous samples because this value is already greatly reduced due to the intrinsic complexity of the atomic structure. However, creating solid solutions is anticipated to have a strong influence on the Seebeck coefficient, which can be tailored to achieve maximum values for the zT and may still have some effect on the thermal conductivity. The results of the Yb-La solid solution study are currently pending publication in the Journal of Electronic Materials [100], while the YbCu_2Si_2 - YbCu_2Ge_2 results are drafted for future publication.

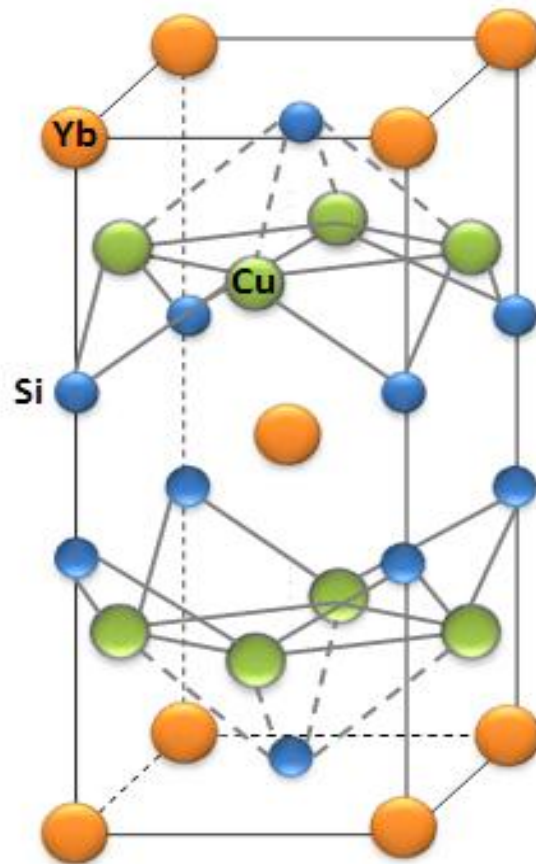


Figure 6-1: Unit cell diagram of YbCu_2Si_2 .

6.2 YbCu₂Si_{2-x}Ge_x

YbCu₂Si₂ is isostructural with YbCu₂Ge₂, and the solid solution between these compounds has been investigated here. This solid solution is interesting because there is no change in the concentration of Yb atoms in the compound, but the size of the unit cell is altered instead by substitution on the Si site. The Ge atom is larger than the Si atom, therefore an expansion in the lattice parameter is expected which can be used to tailor the average Yb valence. Ge is also heavier than the Si atom and thus a reduction in the lattice thermal conductivity is expected.

By expanding the unit cell, the average Yb valence should shift toward a more divalent state from the nominal 2.75 of the pure YbCu₂Si₂ sample. If results from the YbAl₂-ScAl₂ solid solution hold true for other Yb-based intermediate valence compounds, the Seebeck coefficient should be maximized when the average Yb valence is approximately 2.5. The YbCu₂Si₂-YbCu₂Ge₂ solid solution should provide an interesting series on which to evaluate the Seebeck coefficient and its relationship with the average Yb valence.

6.2.1 Synthesis

Samples were formed in the solid solution YbCu₂Si_{2-x}Ge_x where x=0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, and 2.0. Similar to the methods previously utilized, the two base compounds were initially synthesized and then mixed together before densification to form the desired compositions. Both the YbCu₂Si₂ and YbCu₂Ge₂ base compounds were formed by direct arc melting of the stoichiometric quantities. The two base compounds were then powdered and mixed together by ball-milling stoichiometric quantities for 20 minutes and followed by sieving using a 60mesh screen. The powder was then densified using PECS processing at 950°C under 60MPa of pressure for 30 minutes. This time and temperature profile resulted in samples with densities >95% of the theoretical value.

6.2.2 Characterization

Each sample was characterized using XRD, as shown in Figure 6-2. The systematic shift in the large 2θ range toward lower angles as Ge content is increased is characteristic of an expansion in the unit cell. The change in the unit cell volume is plotted in Figure 6-3, showing the linear increase in size as the Ge concentration is increased. Also shown Figure 6-3 is the unit cell volume for each of the end compounds as reported in the literature [92]. The increase in the unit cell volume is the primary driving force for a change in the average Yb valence, and thus the motivation for studying this solid solution.

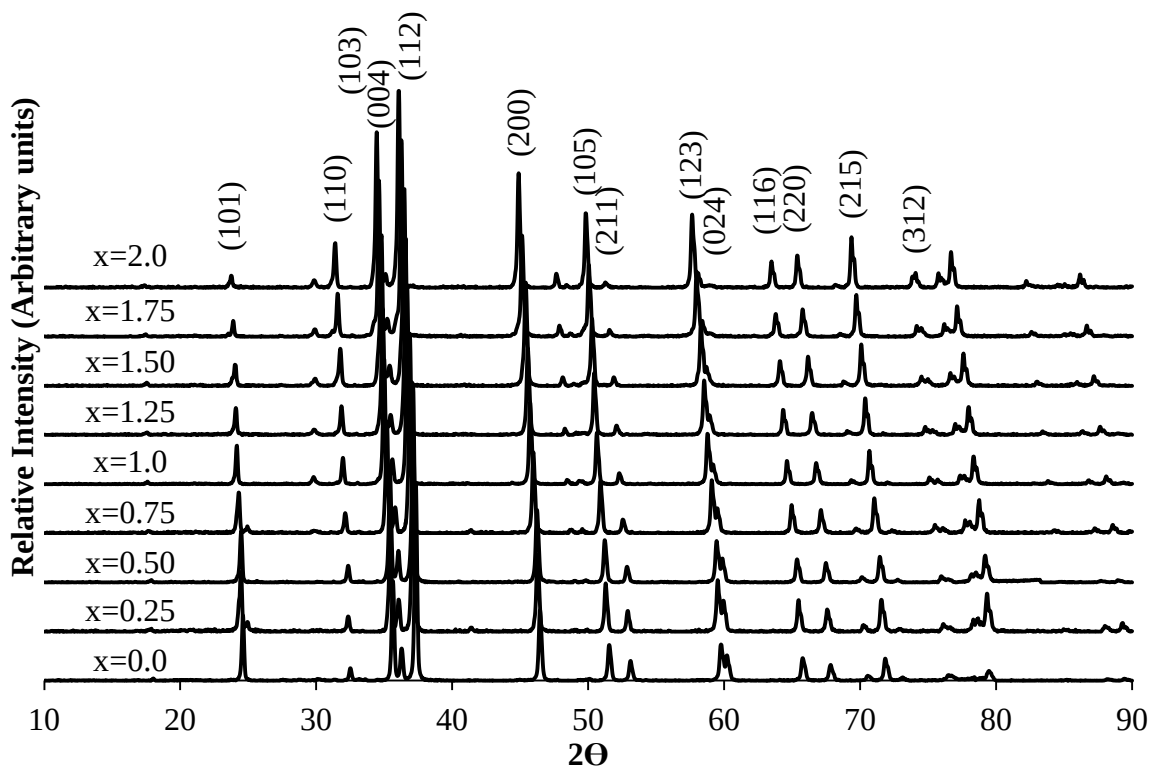


Figure 6-2: XRD patterns for the YbCu₂Si_{2-x}Ge_x solid solution.

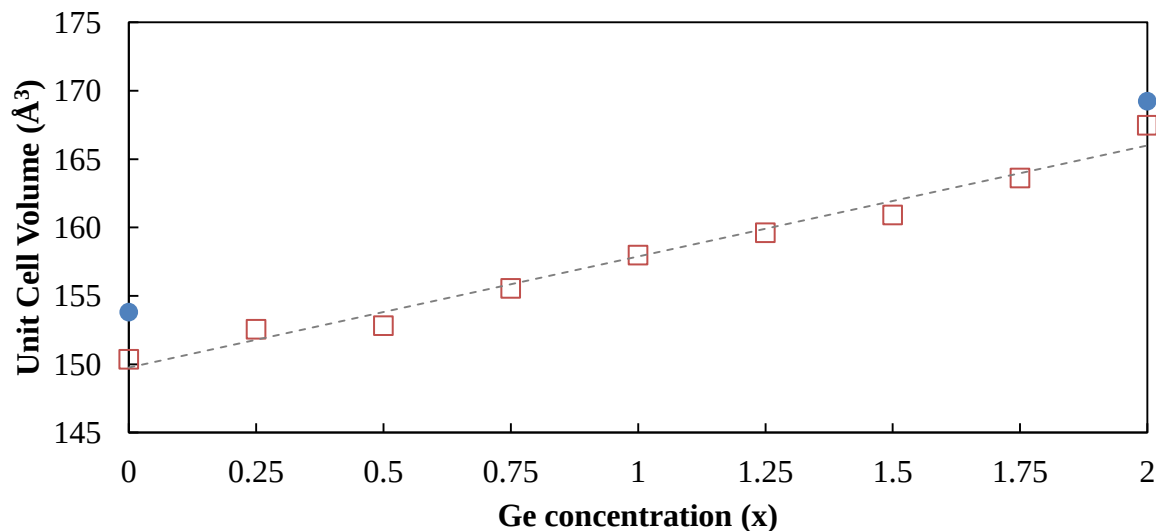
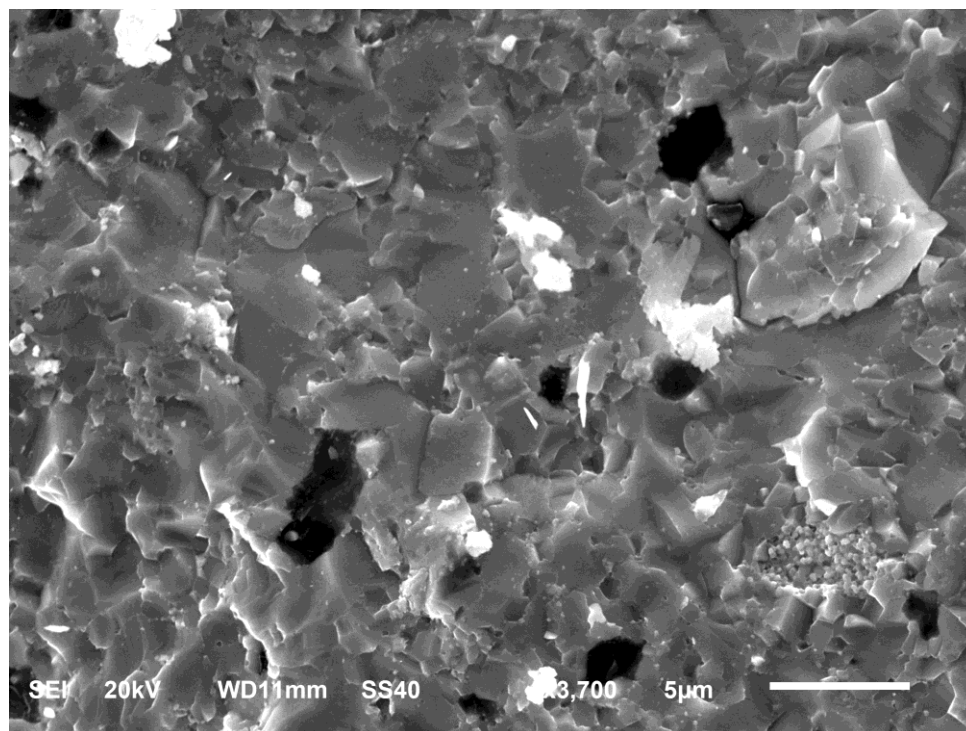


Figure 6-3: The unit cell volume increases linearly as the Ge concentration is increased in the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution. Solid circles represent literature data [92].

Figure 6-4 shows the micrographs for the end compounds YbCu_2Si_2 and YbCu_2Ge_2 collected via SEM. These figures show grain sizes on the order of several microns, consistent with other Yb-based compounds processed in the same manner as discussed in the above chapters. Small quantities of oxygen were observed via EDS even though secondary phases are not visible in the XRD patterns. The amount of oxygen detected here is small and thus can be ignored for the thermoelectric transport properties; however, it is taken into account for the magnetic measurements as discussed in the following sections. The oxide impurity is assumed to be Yb_2O_3 , an impurity commonly found in Yb-based compounds, and qualitatively confirmed by EDS measurements.

A



B

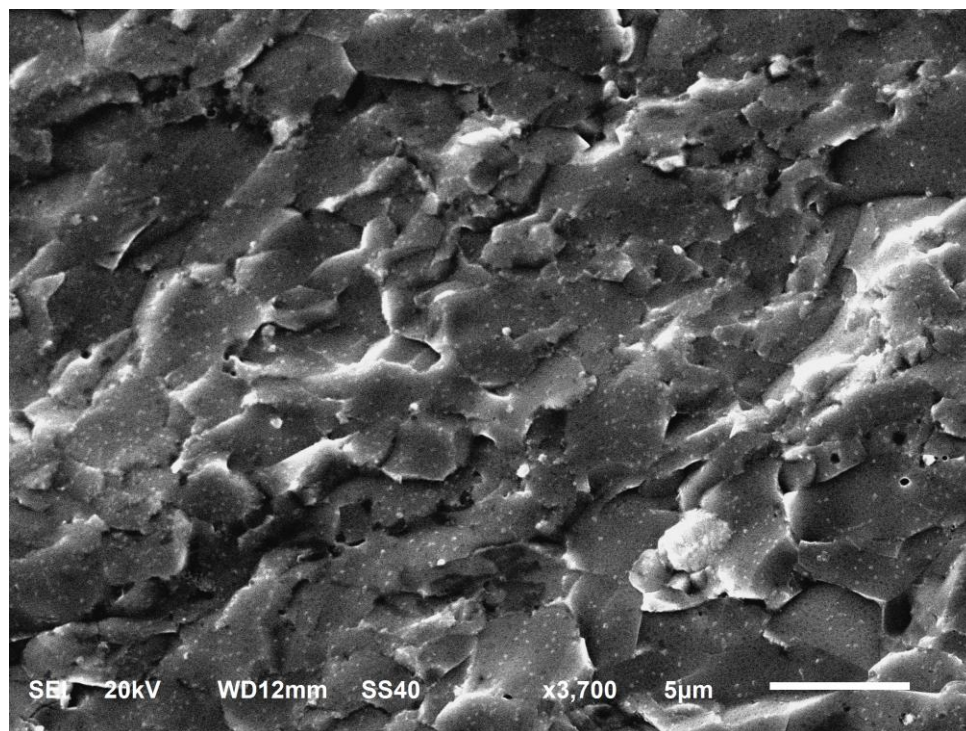


Figure 6-4: SEM images of fractured surfaces for A) YbCu₂Si₂ and B) YbCu₂Ge₂.

6.2.3 Transport Properties

The electrical resistivity of this solid solution decreases systematically as Ge is added to the system as shown in Figure 6-5. The YbCu_2Si_2 sample has a fairly large electrical resistivity compared to some intermediate valence compounds, which is detrimental to the power factor of this base compound. However, the pure YbCu_2Ge_2 sample has a resistivity of approximately $20\mu\Omega\text{cm}$ at room temperature. This reduced electrical resistivity is good for the power factor, but creates a large electronic contribution to the thermal conductivity.

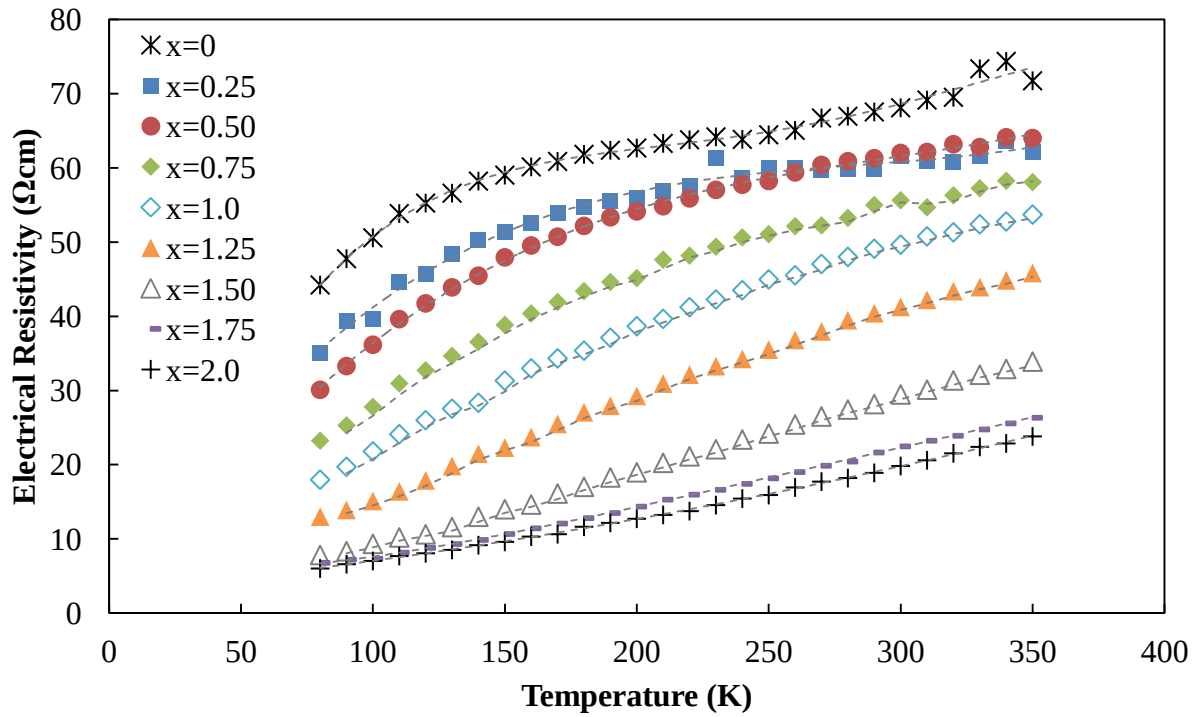


Figure 6-5: The electrical resistivity for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75$ and 2.0 .

Broad maxima in the Seebeck coefficient for each composition are shown in Figure 6-6. As Ge is added to the system, the magnitude of the Seebeck coefficient is reduced and the temperature at which the maxima occur shifts toward a higher temperature. This shift in magnitude toward higher temperatures is opposite of that seen in the $\text{YbAl}_2\text{-ScAl}_2$ solid solution,

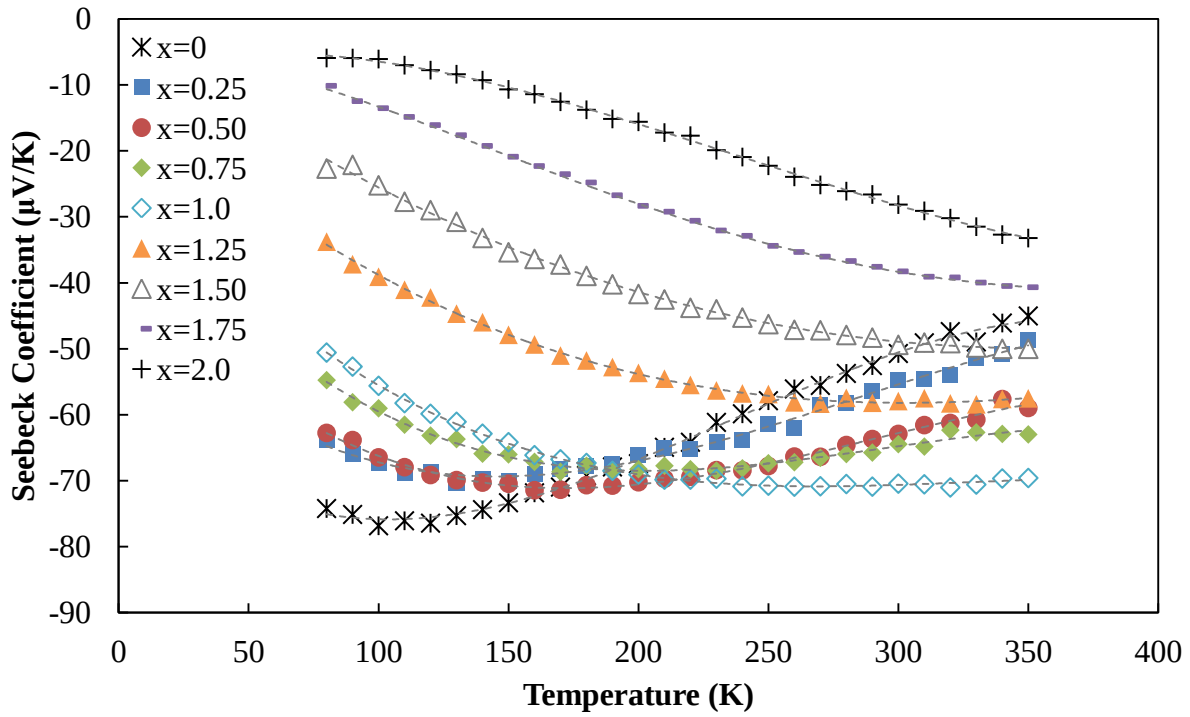


Figure 6-6: The Seebeck coefficient for the YbCu₂Si_{2-x}Ge_x solid solution where x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75 and 2.0.

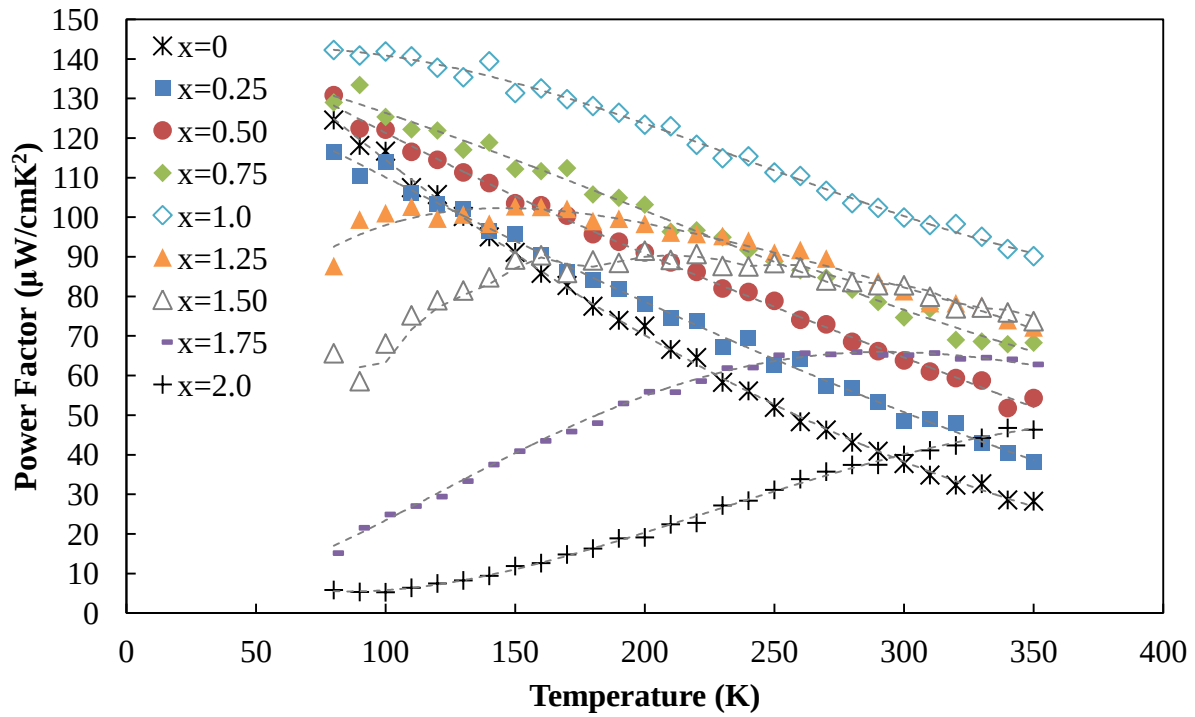


Figure 6-7: The power factor for the YbCu₂Si_{2-x}Ge_x solid solution where x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75 and 2.0.

where the peak of the Seebeck coefficient was shifted towards lower temperatures as the size of the unit cell decreased. This result supports the hypothesis that increasing the unit cell volume has the opposite effect on the temperature dependence of the Seebeck coefficient as compressing the unit cell. Combining the reduction in the electrical conductivity with the diminished Seebeck coefficients, the power factor, shown in Figure 6-7, is enhanced across the entire temperature range for $x \leq 1.0$ and at higher temperatures for higher concentrations of Ge.

Substituting Ge for Si makes that samples more metallic, however the solid solution also increases the phonon scattering rate. The lattice thermal conductivity is reduced as the electronic component increases, resulting in a decrease in the total thermal conductivity for $x < 1.0$ across the entire temperature range, as can be seen in Figure 6-8. The total thermal conductivity is significantly increased in samples with large Ge concentration as the electronic component overwhelms any reduction in the lattice thermal conductivity originating from point defects.

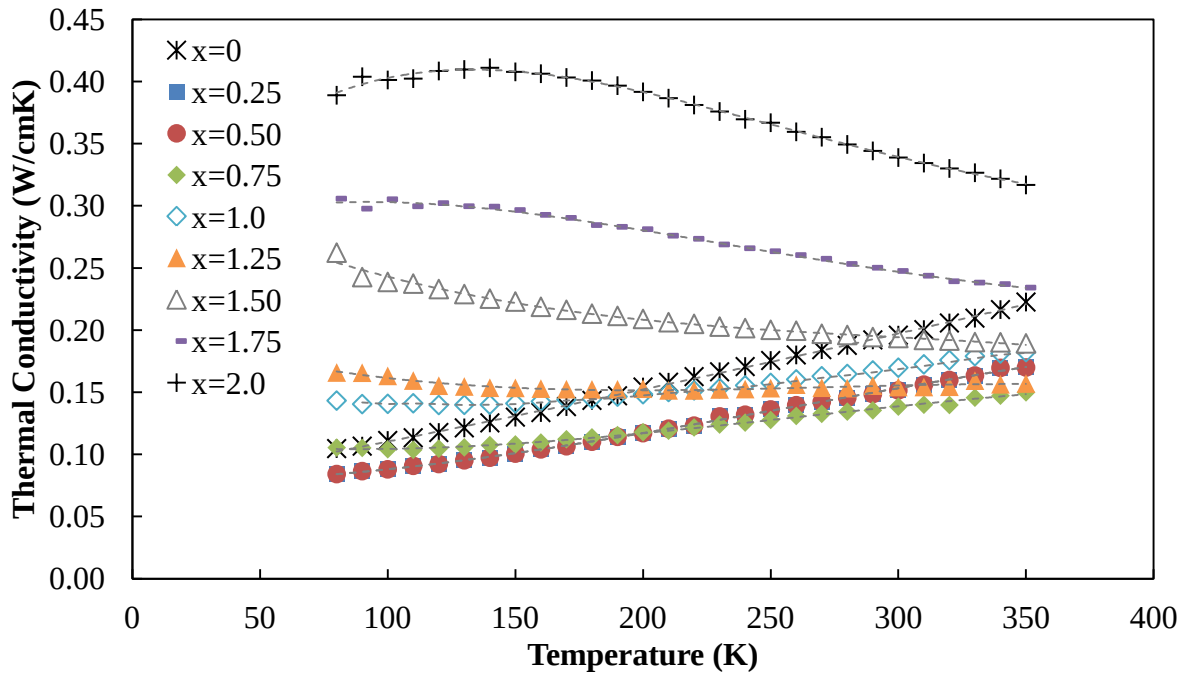


Figure 6-8: The thermal conductivity for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75$ and 2.0 .

The zT for these materials is enhanced for $x \leq 1.0$ resulting from the increased power factor combined with the decrease in the thermal conductivity. Higher concentrations of Ge also result in increased zT when compared to the YbCu_2Si_2 sample, particularly at higher temperatures; however, the values are not as large as those achieved by the $x = 1.0$ sample. By varying the Ge content, a maximum zT of 0.16 can be achieved across the temperature range 150K to 350K, as seen in Figure 6-9.

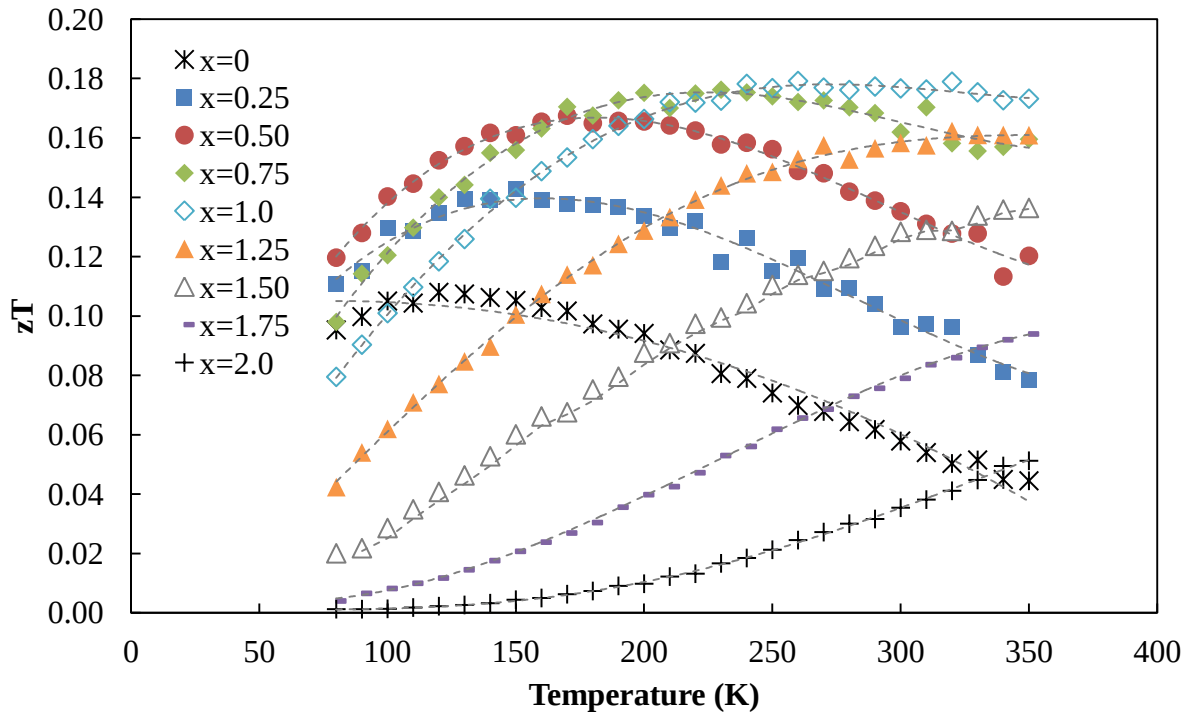


Figure 6-9: The zT for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $x = 0, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75$ and 2.0 .

6.2.4 Magnetic Properties

The expansion of the unit cell is suspected to cause a change in the average Yb valence, which can be determined by fitting the ICF model to the magnetic susceptibility. The magnetic moment

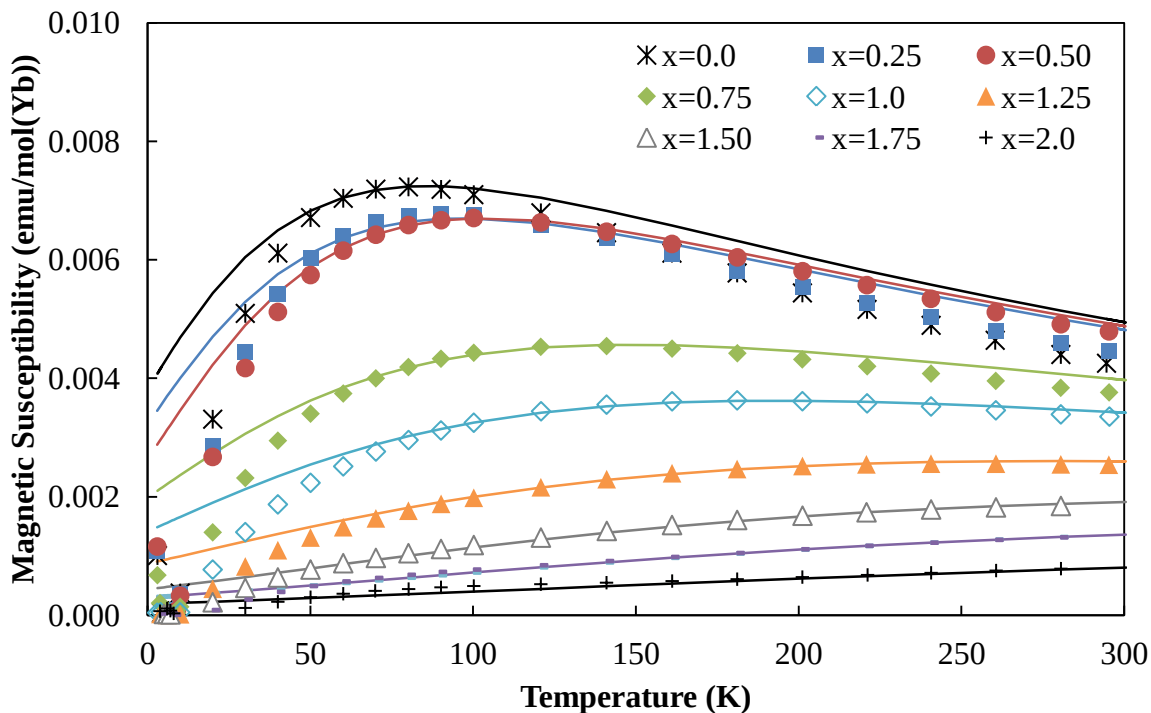


Figure 6-10: The corrected magnetic susceptibility for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $0 \leq x \leq 2$. Solid lines are fits to the ICF model.

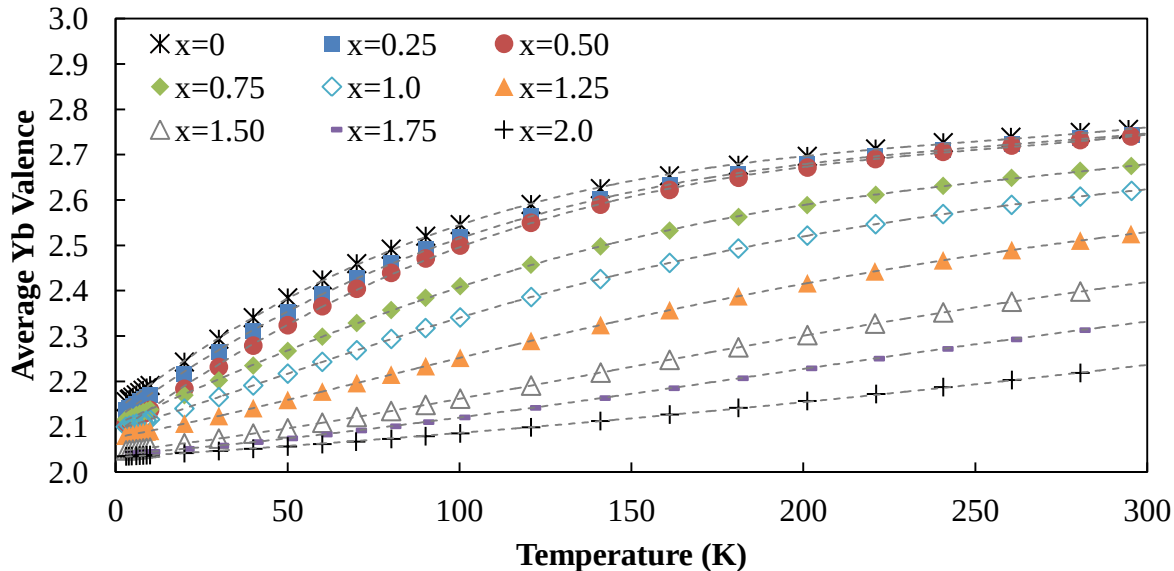


Figure 6-11: The average Yb valence as a function of temperature for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $0 \leq x \leq 2$.

was collected for each sample and then corrected for a small quantity of Yb_2O_3 , as determined by fitting the low temperature Curie tail. After removing this background, the resulting magnetic

susceptibility per mole of Yb is shown in Figure 6-10, along with the ICF model fits. The peak in the magnetic susceptibility shifts towards higher temperatures as the Ge concentration is increased. Figure 6-11 shows a decrease in the average Yb valence across the entire temperature range as the Ge content is increased, as hypothesized for an expansion in the unit cell. This plot also shows a relatively flat trend near an average Yb valence value of 2.5, particularly for the $x=1.0$ sample, explaining the large broad peaks observed in the Seebeck coefficient.

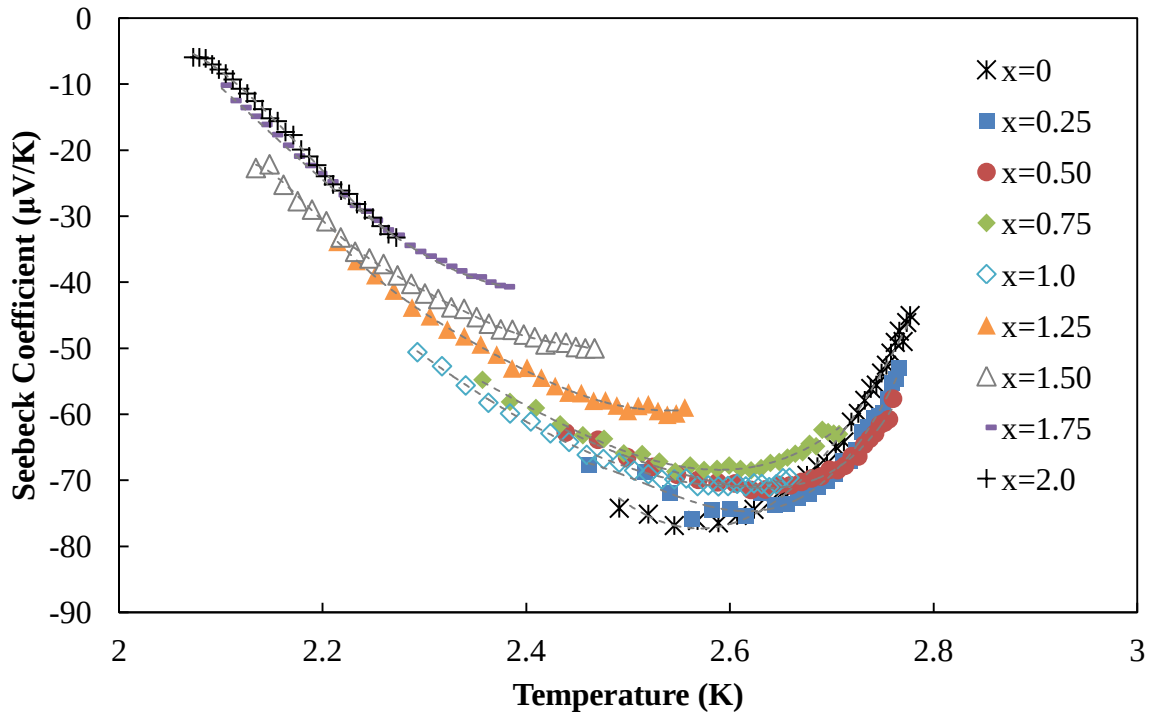


Figure 6-12: The Seebeck coefficient vs. average Yb valence for the $\text{YbCu}_2\text{Si}_{2-x}\text{Ge}_x$ solid solution where $0 \leq x \leq 2$.

The fits from the ICF model were used to compare the average Yb valence and the Seebeck coefficient data, as shown in Figure 6-12. This figure supports the results found in the $\text{YbAl}_2\text{-ScAl}_2$ solid solutions, where the Seebeck coefficient is maximized in each composition when the average Yb valence is near 2.5. The shift in the temperature at which the Seebeck coefficient peaks is also related to the temperature at which the magnetic susceptibility peaks, as

shown in Figure 6-13. This result further supports the strong relationship between the Seebeck coefficient and the magnetic state of the Yb atoms in the compound.

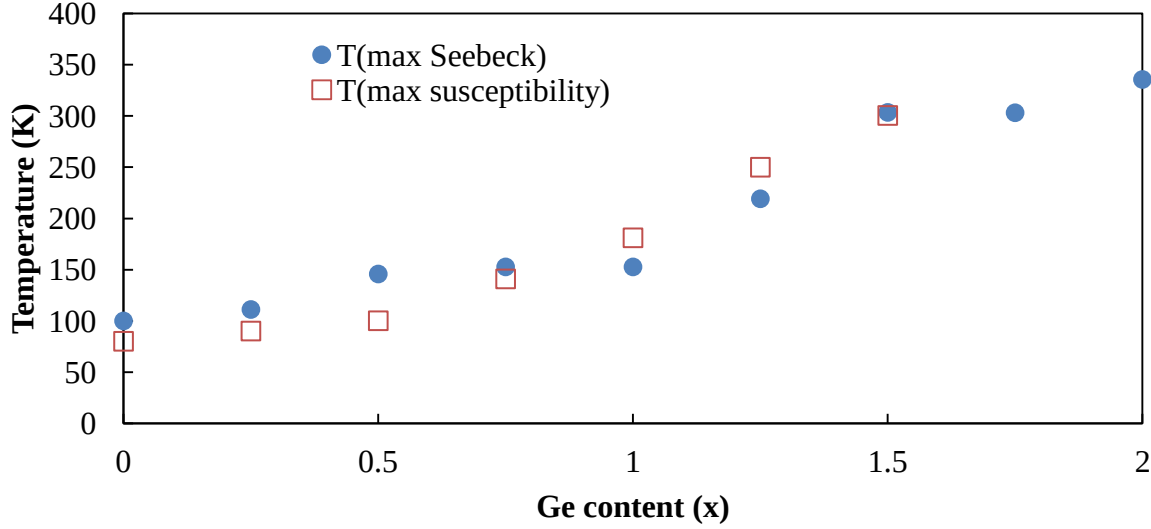


Figure 6-13: Comparison of the temperatures at which the magnitude of the Seebeck coefficient and the magnetic susceptibility are maximized as a function of Ge concentration.

6.3 Yb_{1-x}La_xCu₂Si₂

6.3.1 Synthesis

The solid solution Yb_{1-x}La_xCu₂Si₂ where x=0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95, and 1.0 were synthesized by first forming the two ternary compounds, YbCu₂Si₂ and LaCu₂Si₂, independently. These base compounds were synthesized by arc melting stoichiometric quantities of the elements. The LaCu₂Si₂ compound was homogenized via heat treatment after the arc melting process, and then ball milled. This high temperature homogenization process was done in for 48 hours at 750°C. Stoichiometric quantities of the base ternary compounds were balled milled together for 20 minutes to achieve the correct composition. The powder was then sieved and densified using PECS processing. PECS was done under 60MPa of pressure at a temperature of 950°C for 30 minutes.

6.3.2 Characterization

X-ray diffraction was done following each step of the synthesis process. The final XRD patterns for select compositions in the solid solution are reported in Figure 6-14. XRD patterns were also collected on the other compositions, which show only the characteristic peaks with no visible secondary phase, but were not included here in order to simplify the plot. A shift in the peaks is clearly visible at higher angles, indicating a change in the size of the unit cell. The unit cell volume for each composition is shown in Figure 6-15, consistent with the literature data for the base compounds YbCu_2Si_2 [92] and LaCu_2Si_2 [101] represented as filled circles.

The microstructure of the LaCu_2Si_2 is shown in Figure 6-16. The grains shown here are on the order of several microns in diameter and appear to be similar to the YbCu_2Si_2

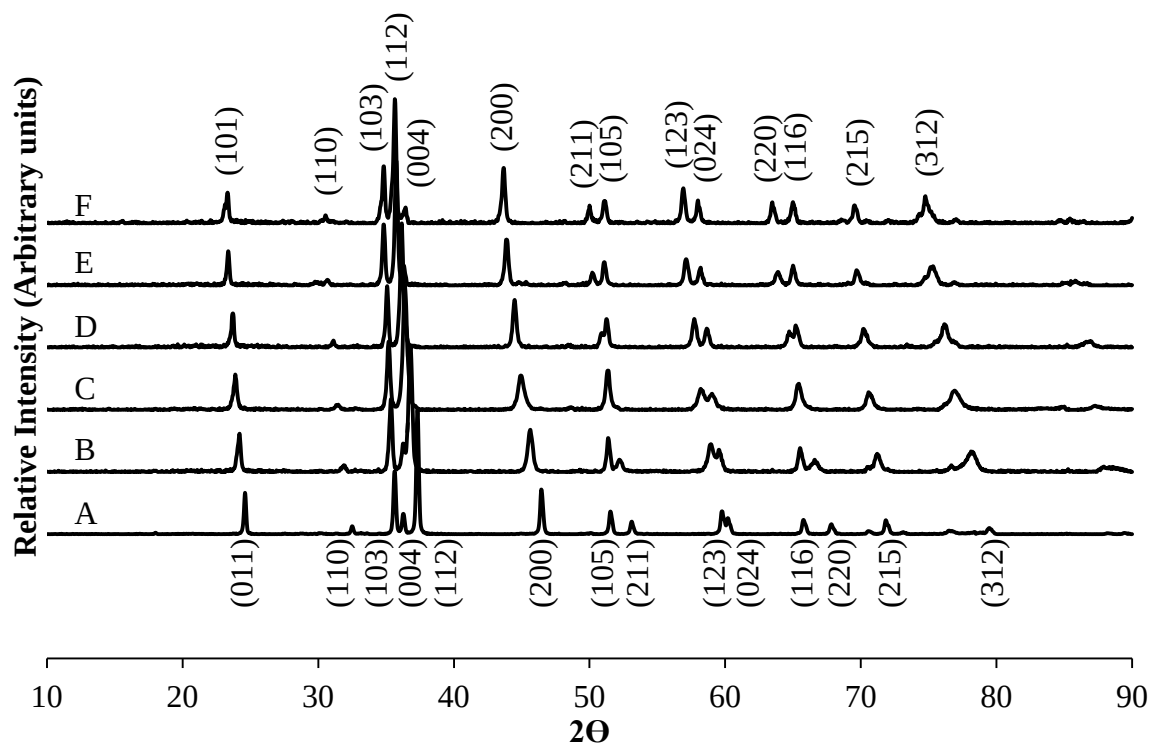


Figure 6-14: XRD patterns collected at room temperature for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where A) $x = 0$, B) $x = 0.20$, C) $x = 0.40$, D) $x = 0.60$, E) $x = 0.80$, and F) $x = 1.0$.

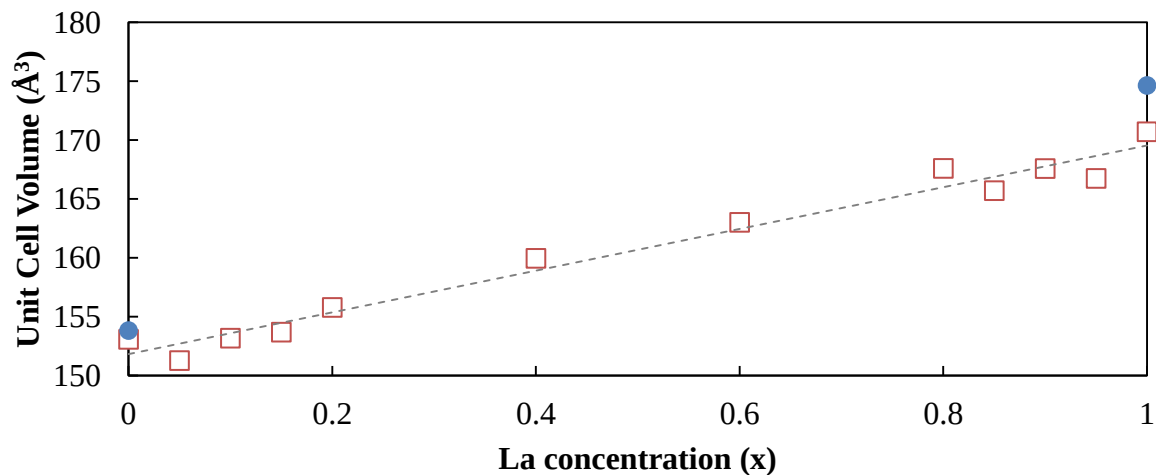


Figure 6-15: The unit cell volume increases linearly as the La concentration is increased in the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution. Solid circles represent literature data.

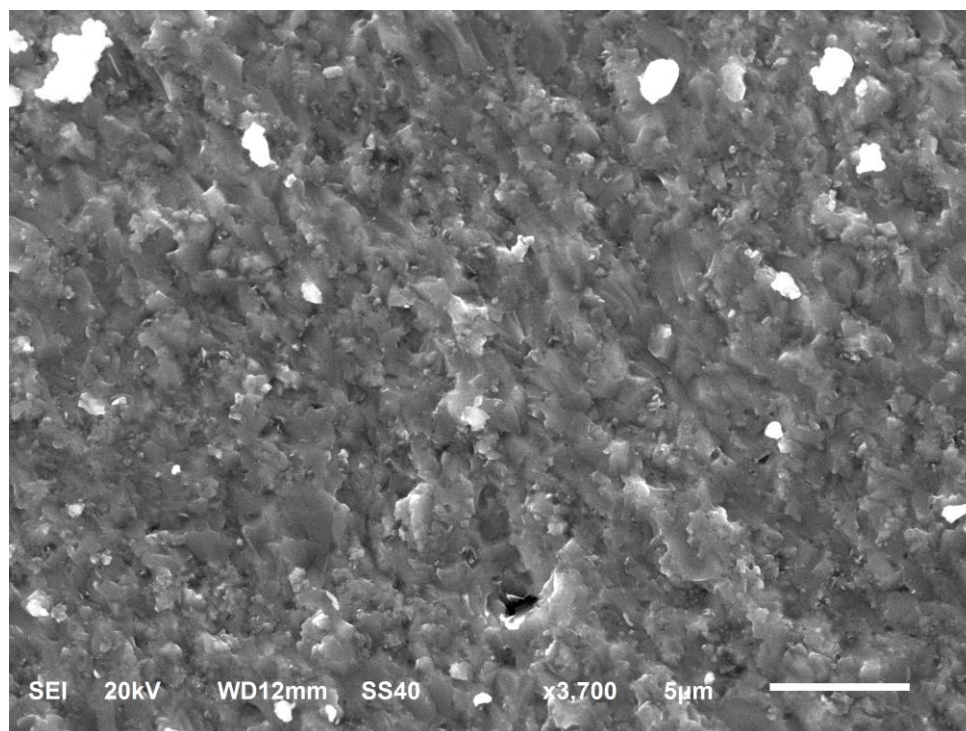


Figure 6-16: SEM images of fractured surfaces for LaCu_2Si_2 .

microstructure. Small impurity phases are noticeable in the SEM images although the XRD patterns do not show any extraneous peaks. Again, these impurities are oxide phases and are assumed to be less than 5% based on the limitations of XRD.

6.3.3 Transport Properties

The electrical resistivities of these samples is not affected much by low concentrations of La, however moderate quantities ($x > 0.20$) causes a significant drop in the electrical resistivity, as can be seen in Figure 6-17. The pure LaCu_2Si_2 sample has a different trend in the resistivity than the samples with even dilute Yb concentrations. It is suspected that the magnetic moment of the Yb atom allows the electrical resistivity to become very small, an effect that is not observed in LaCu_2Si_2 .

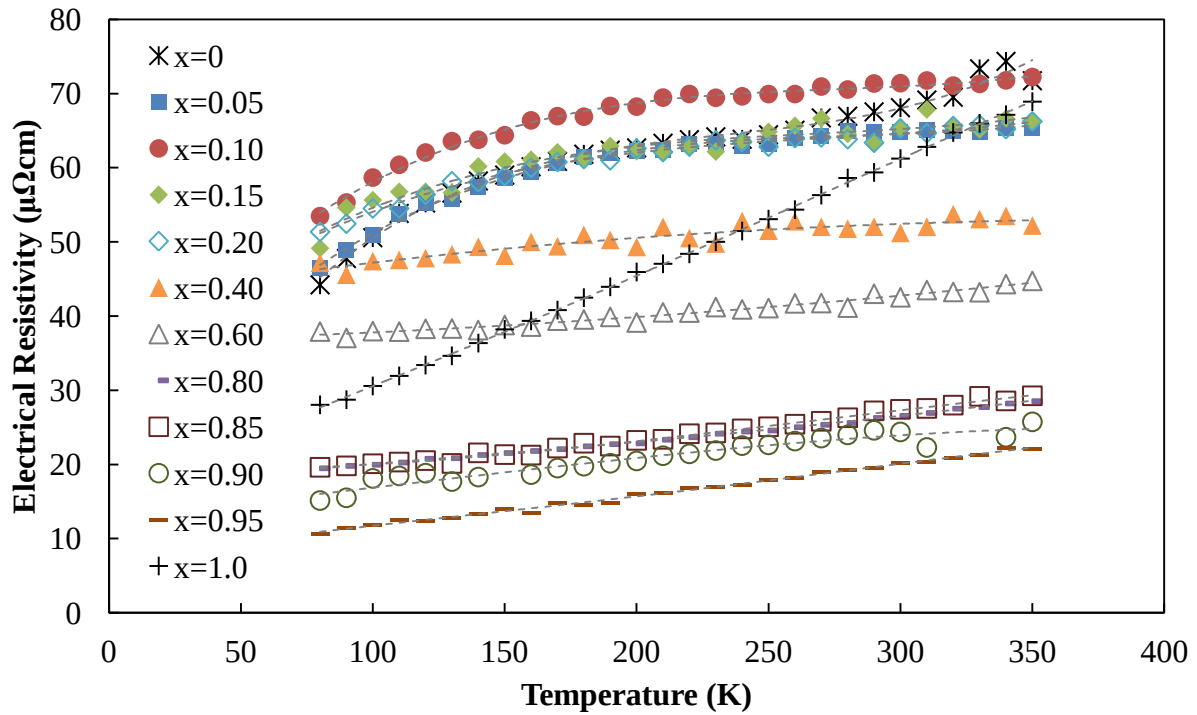


Figure 6-17: The electrical resistivity for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95$, and 1.0 .

The Seebeck coefficient data shown in Figure 6-18 reveals that it is strongly dependent on the La concentration, and as La is added to the composition, the magnitude of the Seebeck coefficient decrease. However, as the La concentration increases, it is also apparent that the

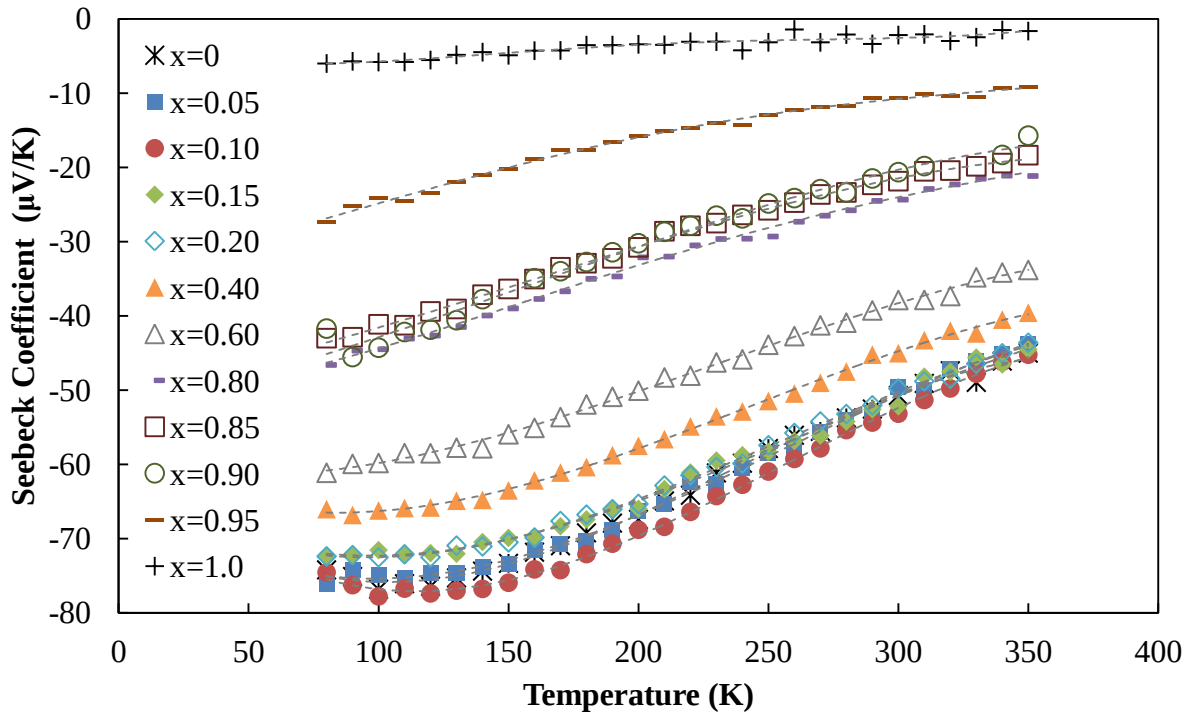


Figure 6-18: The Seebeck coefficient for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95$, and 1.0 .

temperature at which the Seebeck coefficient peaks is shifted towards lower temperatures. The Seebeck coefficient must approach the origin at zero Kelvin, therefore the peaks for high concentrations of La are assumed to occur below the measured temperature. While the magnitude of the Seebeck coefficient decreases with increased La, this reduction is relatively small in samples with La concentrations up to $x=0.60$. Therefore it is possible to optimize the temperature and magnitude of the Seebeck coefficient by tuning the La concentration.

Because there is little change in the electrical resistivity and Seebeck coefficient at low La concentrations, the power factor is not dramatically changed, as can be seen in Figure 6-19. In the previous chapters, a reduction to the electrical resistivity has been beneficial to the power factor; however, in this case while the electrical resistivity is reduced with increasing La concentrations, the Seebeck coefficient is also reduced. Thus a reduction in the power factor is

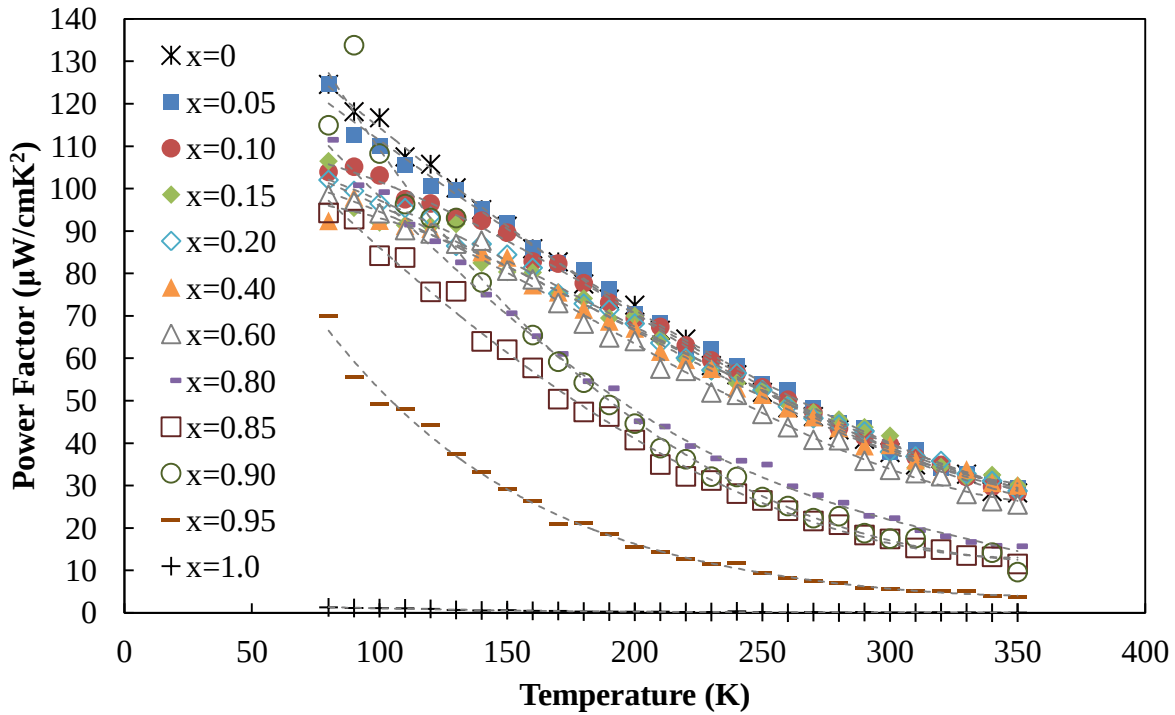


Figure 6-19: The power factor for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95$, and 1.0 .

observed for large concentrations of La substitution.

Creating solid solutions has also been a successful method for reducing the lattice thermal conductivity of samples. Unfortunately, once again the thermal transport in these samples is dominated by the electronic component rather than lattice component, and is therefore much more strongly related to the electrical conductivity, which was shown above to be very large. Using the Weidemann-Franz law, it is possible to calculate the electronic contribution, which is nearly 90% of the total thermal conductivity. As La is added to the system the lattice thermal conductivity is reduced; however, electronically the samples become more metallic, thus, the thermal conductivity gets much larger, particularly in the high La concentration samples, shown in Figure 6-20. Small concentrations of La do slightly reduce the lattice thermal conductivity while the electronic resistivity is not significantly changed, therefore a small

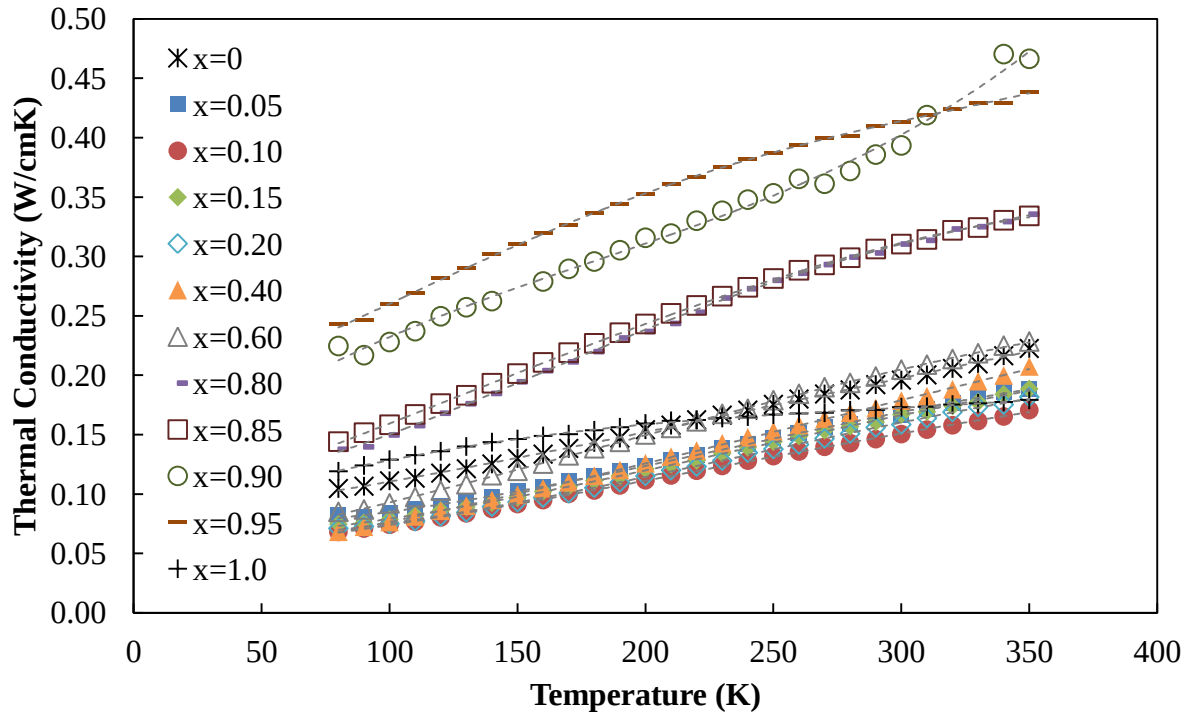


Figure 6-20: The thermal conductivity for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95$, and 1.0 .

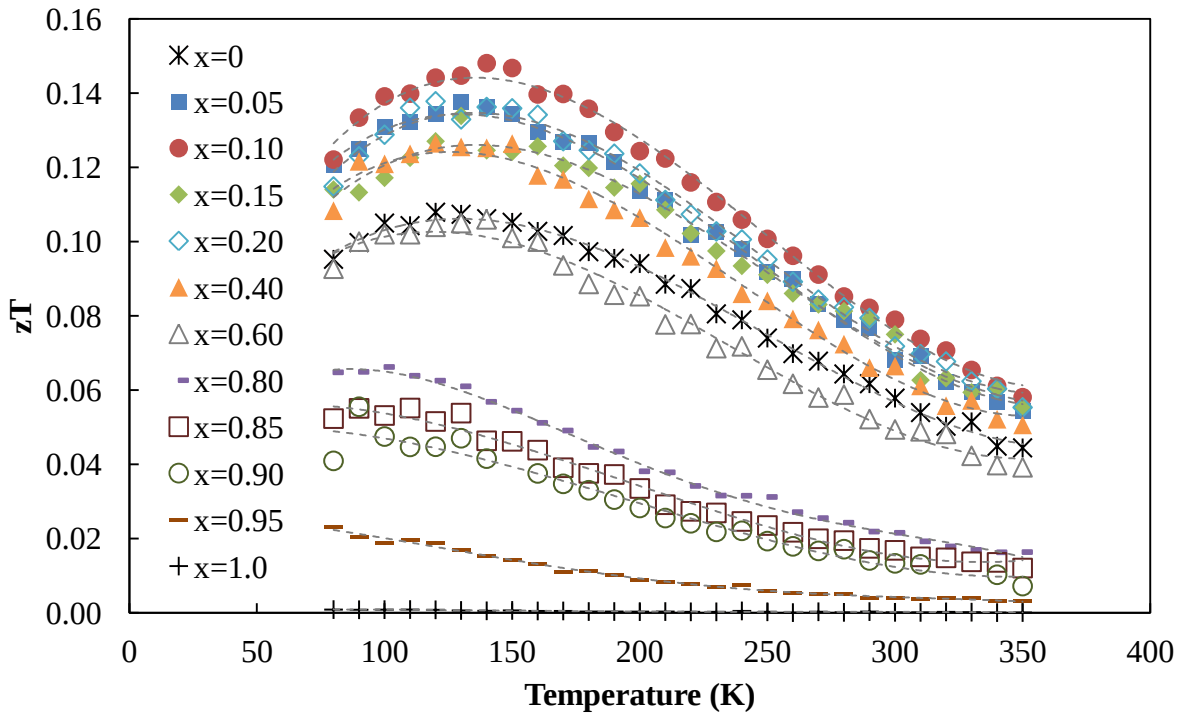


Figure 6-21: The zT for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95$, and 1.0 .

reduction in the total thermal conductivity can be seen for samples with La concentration $x \leq 0.40$, particularly in the low temperature region.

Combining these transport properties, the dimensionless figure of merit is shown in Figure 6-21. The peak of the zT reflects the shift towards lower temperatures in the Seebeck coefficient, as expected. More significantly, this plot demonstrates that small concentrations of La give the best results, reaching zT values of nearly 0.15 at 150K. While this value is enhanced from the pure YbCu_2Si_2 sample and does show a fairly broad peak, it is not as large as that achieved by the Ge substitution and the large electronic contribution to the thermal conductivity is once again the limiting factor in the potential for this material as a thermoelectric.

6.3.4 Magnetic Properties

In order to better understand the peak in the magnitude of the Seebeck coefficient, measurements were performed to collect the magnetic moment. This data was again corrected for an oxide impurity phase which contributes a paramagnetic moment to the background. The corrected moment was used to find the magnetic susceptibility of each of the samples and then fit to the ICF model to extract the average Yb valence. Figure 6-22 shows that as the La concentration is increased the magnetic signal is significantly decreased because the Yb concentration is small. Therefore, these compositions were very difficult to fit to the model, which requires strong signals from the Yb atoms. Samples with small concentrations of La were investigated; however the corrected data used to obtain the average Yb valence was only reliable for samples $x \leq 0.20$. As can be seen in Figure 6-23, increasing temperature causes an increase in the average Yb valence from 2.2 to 2.8, contradictory to the literature, which suggests that the Yb valence has a much flatter trend, growing from ~ 2.5 to 2.8 [40]. This discrepancy can be assumed to originate from the correction factor and any error in the fits to the model which may

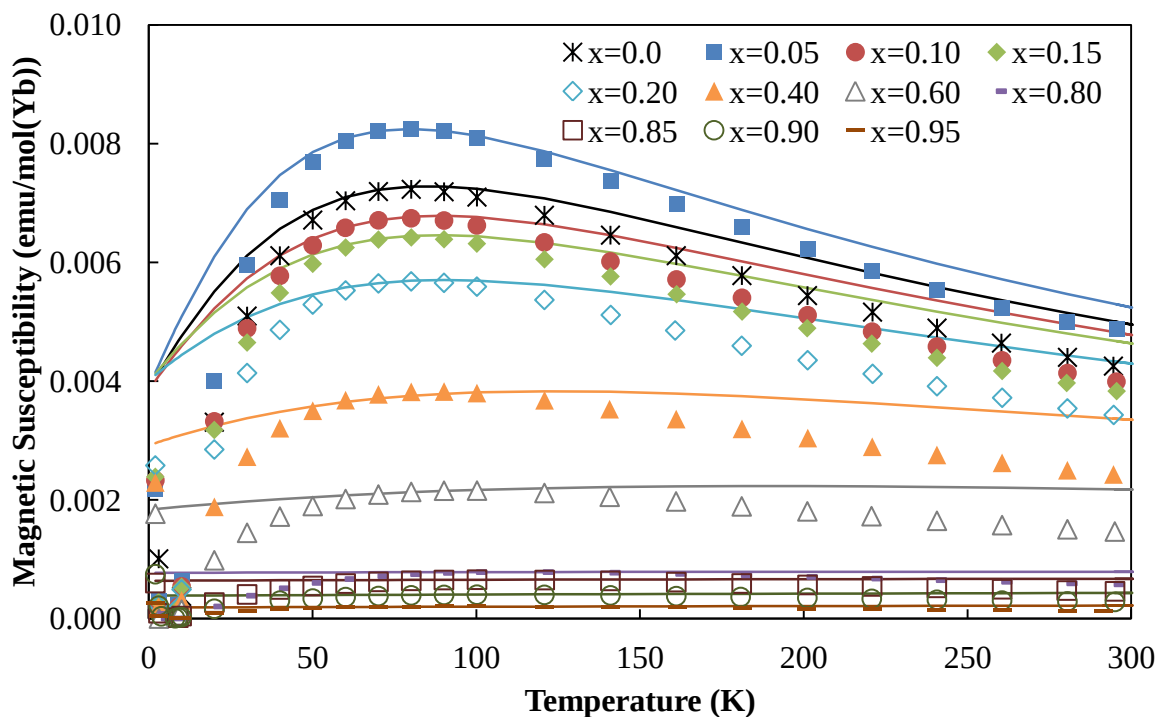


Figure 6-22: The corrected magnetic susceptibility for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.60, 0.80, 0.85, 0.90, 0.95$, and 1.0 .

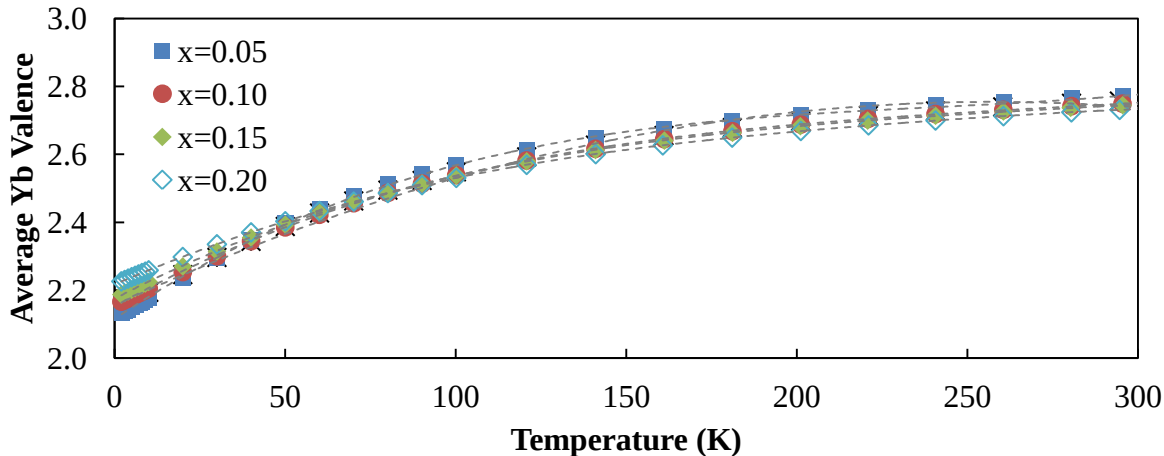


Figure 6-23: The average Yb valence as calculated from the ICF model from 2K to 300K for $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ where $x = 0, 0.05, 0.10, 0.15$, and 0.20 .

arise from this correction. One may readily notice that the fits are quite poor when compared to those reported above on the $\text{YbAl}_2\text{-ScAl}_2$ and $\text{YbCu}_2\text{Si}_2\text{-YbCu}_2\text{Ge}_2$ solid solutions. However, it is still possible to assume that the trend in the average Yb valence from smaller to larger values

is accurate as there is little change in the trends for all of the $x \leq 0.20$ samples and the Seebeck is also maintained in each of these compositions. Assuming these values for the average Yb valence are accurate, Figure 6-24 shows again that the magnitude of the Seebeck coefficient is maximized when the average Yb valence is near 2.5. The Seebeck coefficient is associated with average Yb valences near or above 2.5 because an average Yb valence of less than 2.5 is only observed below 80K, a temperature range in which the transport properties are not measured. The trend observed here may be considered further evidence in support of the previous findings regarding the relationship between the average Yb valence and the Seebeck coefficient.

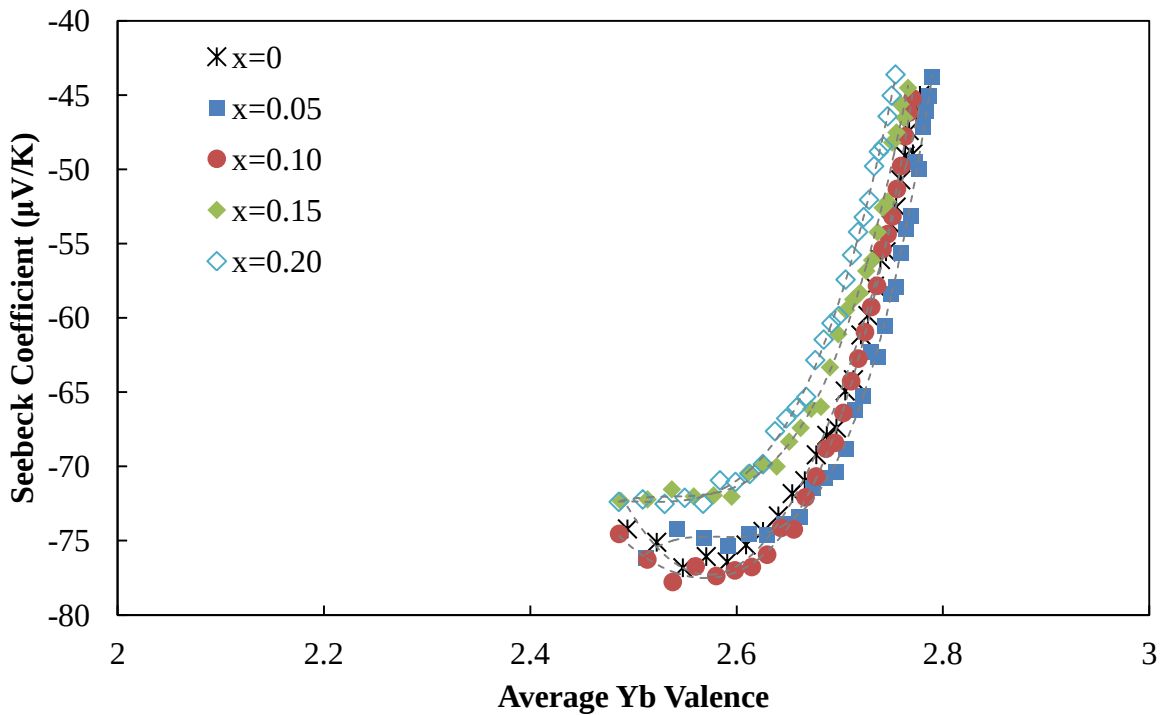


Figure 6-24: The Seebeck coefficient as a function of the average Yb valence for the $\text{Yb}_{1-x}\text{La}_x\text{Cu}_2\text{Si}_2$ solid solution where $x = 0, 0.05, 0.10, 0.15,$ and 0.20 .

6.4 Summary

YbCu_2Si_2 was alloyed with YbCu_2Ge_2 and LaCu_2Si_2 in an attempt to further investigate the effects of chemical substitutions on the average Yb valence and the corresponding changes to the Seebeck coefficient. These substitutions caused an expansion in the unit cell, providing more space for the Yb atoms. This increased lattice parameter was expected to decrease the average Yb valence, as Yb^{2+} has a larger radius than Yb^{3+} . The magnetic susceptibility of these solid solutions was collected and fit to the ICF model to extract the average Yb valence. XRD of the $\text{YbCu}_2(\text{Si},\text{Ge})_2$ solid solution showed that unit cell was expanded and the magnetic fits demonstrated a decrease in the average Yb concentration as Ge was added to the system. In the La solid solution, the lattice parameter was also increased with increasing La content as seen in XRD; however, the dispersion of Yb atoms causes a reduced signal in the magnetic moment and the average Yb valence could not be accurately determined.

The substitutions of Ge and La have opposing affects on the shift in the peaks of the Seebeck coefficient. The $\text{YbCu}_2(\text{Si},\text{Ge})_2$ solid solution shows a shift towards higher temperatures in the peak Seebeck coefficient as Ge content is increased. This shift can be explained by looking at the temperature at which the average Yb valence is near 2.5. Since the average Yb valence decreases with increasing Ge content, a higher temperature is required to achieve a value near 2.5. The Seebeck coefficient of the La substituted samples shows a shift towards lower temperatures, more similarly to that seen in the $\text{YbAl}_2\text{-ScAl}_2$. It is suspected that this shift towards lower temperatures is a result of the dilution of Yb atoms, as proposed by Zlatić and Monnier [34]. However, the lack of reliable results on the average Yb valence prevents a complete explanation for this trend in Seebeck coefficient toward lower temperatures.

The Ge substitution in the YbCu_2Si_2 solid solution not only shifts the peak in the Seebeck coefficient towards higher temperatures, but it also alters the electrical and thermal conductivities. The power factor reaches a maximum value of $140\mu\text{W}/\text{cmK}^2$ at 80K for the $x=1.0$ sample (YbCu_2SiGe). The large thermal conductivity of this sample does not make it the optimal composition across the entire temperature range. Instead, lower Ge concentrations ($x=0.50$) have the best zT at the lowest temperature ranges, while $x=1.0$ is ideal above 200K. A zT value of approximately 0.15 can be achieved at 100K and above using varying compositions where $x \leq 1.0$.

Substitution of La for Yb in the YbCu_2Si_2 compound alters each of the thermoelectric properties in a way that enhances the zT for low La concentrations, reaching values of 0.15 at 150K. Smaller concentrations of La result in the lowered thermal conductivities while the power factors are slightly enhanced due to the reduced electrical resistivity. However, none of these La substituted samples exceed the zT values of those seen in the Ge solid solution.

While the zT values are enhanced from that of the original YbCu_2Si_2 sample, they are still not sufficiently large for most applications. However, the broad peak in the zT that can be achieved by varying concentrations of Ge or La is potentially valuable for niche Peltier cooling applications. Unfortunately there is little work that could be done further enhance this zT because most of the thermal conductivity comes from the electronic contribution due to the already complex unit cell. Therefore, grain size engineering and further isoelectronic substitution would be unlikely to significantly reduce the lattice thermal conductivity. Thus the only remaining method for increasing the zT is further enhancement of the power factor.

Chapter 7 Conclusions

The goal of this work was to synthesize new materials using common processing techniques through which the thermoelectric properties could be controlled by chemical substitution. Yb-based compounds were investigated because of their unique properties in the cryogenic temperature range, an area that has not been heavily investigated. By studying the unique intermediate valence behaviors that many Yb-based materials exhibit it is possible to control the thermoelectric properties via a newfound understanding of the underlying physical concepts and their dependence on temperature and stoichiometry.

Synthesis of these Yb-based materials required an innovative approach due to the volatility of pure Yb metal. As discussed in Chapters 4 and 5, new methods which required non-stoichiometric quantities of the constituent elements resulted in high-purity samples. The trialuminide compounds were formed using an aluminum flux arc melting method which prevented the dialuminide phase from crystallizing as the sample cooled from the molten phase. This excess aluminum was then removed via chemical etching leaving porous chunks of pure YbAl_3 which were then powder processed and sintered. The dialuminide samples discussed in Chapter 5 was formed by arc melting with excess Yb to compensate for the non-homogenous losses that occur during the arc melting process. A high temperature heat treatment allowed any remaining Yb metal to vaporize and only the desired YbAl_2 phase remained. These samples were also powder processed and densified. These two new synthesis techniques allowed high purity polycrystalline samples (particularly in comparison to the polycrystalline samples previously reported in the literature) to be investigated.

Thermoelectric properties were measured on three different series of solid solutions. YbAl_3 was alloyed with ScAl_3 , ErAl_3 and LuAl_3 resulting in increased power factor and zT values for each solid solution where 25% of the Yb atoms were substituted. The solid solution between YbAl_2 and ScAl_2 showed unique peaks in the Seebeck coefficient near 50K, particularly for samples with large quantities of Sc. These peaks greatly enhanced the zT value in the cryogenic temperature range. The peak in the Seebeck coefficient also shifted toward lower temperatures as the Sc content was increased. These dialuminide samples were further investigated via magnetic property measurements in order to evaluate the average Yb valence in the range where the magnitude of the Seebeck coefficient was largest. This investigation revealed a strong relationship between the peak temperatures of the Seebeck coefficient and the magnetic susceptibility as well as between the maximum Seebeck coefficient and an average Yb valence of approximately 2.5. The final series that was investigated in this work was the YbCu_2Si_2 series in which solid solutions with YbCu_2Ge_2 and LaCu_2Si_2 were formed. An increase in the zT was observed in the YbCu_2Si_2 - LaCu_2Si_2 solid solution at low temperatures, while the zT of the YbCu_2Si_2 - YbCu_2Ge_2 samples were enhanced across the entire temperature range. The peak in the Seebeck coefficients of these two solid solutions behaved in different manners, where Ge caused the peak to shift towards higher temperatures, the La substitution caused a shift toward lower temperatures. The average Yb valence of these compounds was determined using magnetic data. Reminiscent of the dialuminide series, the temperature at which the Seebeck coefficient is maximized matches closely with the temperature at which magnetic susceptibility peaks. Also, the magnitude of the Seebeck coefficient is maximized when the average Yb valence is near 2.5.

These results provide evidence that the Seebeck coefficient is maximized when the f-shell electrons are in a state of maximum fluctuation, a state which may be achieved by tailoring the unit cell volume through chemical substitution. This chemical substitution causes an expansion or contraction of the unit cell and as the unit cell volume is altered, the Yb atom adapts to the new environment and adjusts the number of electrons in the f-shell. If the volume is reduced the Yb atom loses an electron to better fit into the available space, thus becoming more trivalent, while if the volume is increased the Yb atom becomes more divalent as it retains a full f-shell. This trend is clearly shown in Figure 7-1 where the average Yb valence is plotted vs. the unit cell volume for the $\text{YbAl}_2\text{-ScAl}_2$ solid solution as well as both the of the YbCu_2Si_2 solid solutions.

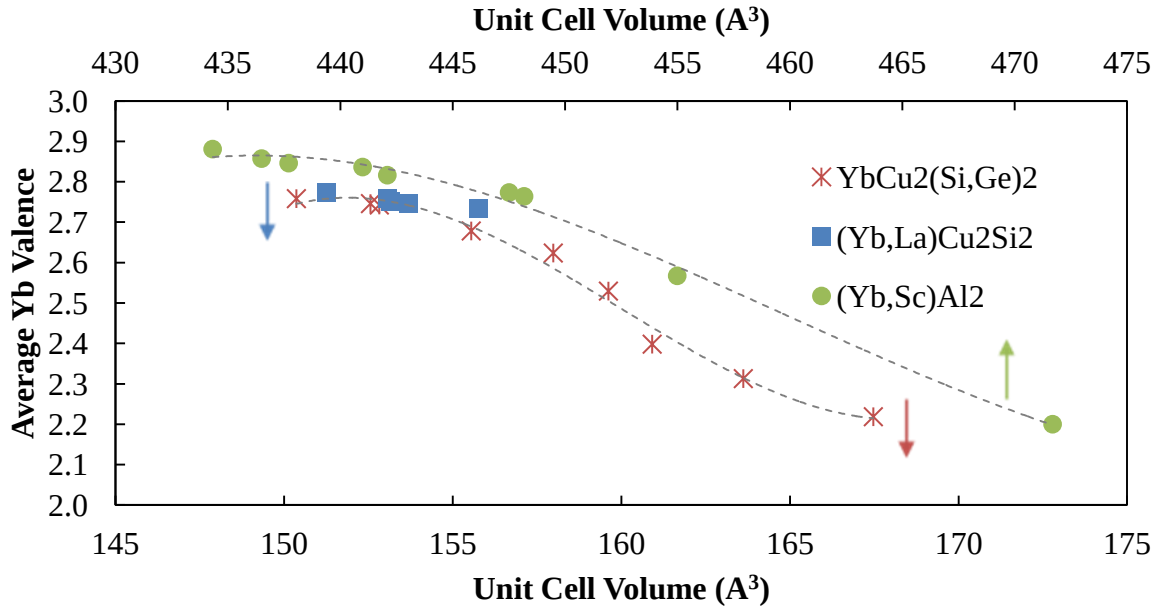


Figure 7-1: The average Yb valence vs. the unit cell volume for three solid solutions shows that the Yb valence state is dependent on the available space in the unit cell.

This figure shows a non-linear relationship in which the average Yb valence transforms from nearly trivalent to the divalent state as the unit cell volume is increased. This trend is apparent in the two solid solutions that were fully studied and limited results from the $\text{YbCu}_2\text{Si}_2\text{-LaCu}_2\text{Si}_2$

solid solution also support this relationship. This figure provides conclusive evidence that the average Yb valence of these systems can be controlled by altering the unit cell volume via chemical substitutions, a method which may be utilized in future work on intermediate valence compounds.

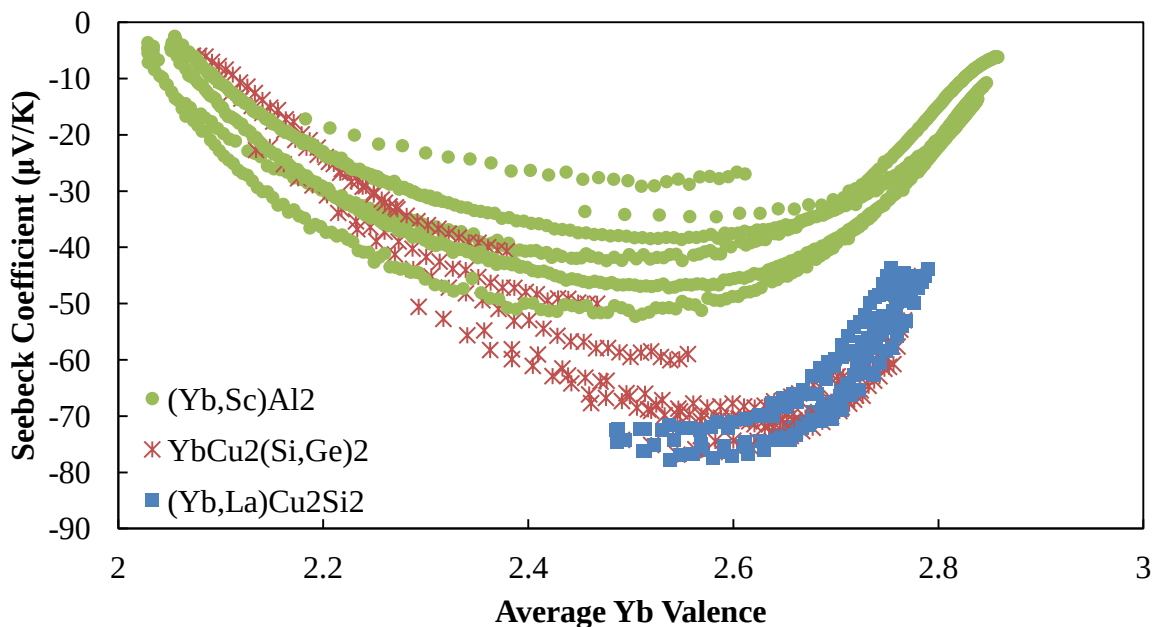


Figure 7-2: The Seebeck coefficient vs. average Yb valence for each of the Yb-based intermediate valence compounds investigated in this work.

It has been well established that the Seebeck coefficient is strongly correlated with the average Yb valence. This correlation is explicitly shown in Figure 7-2, where the absolute value of the Seebeck coefficient is maximized for each solid solution when the average Yb valence is near 2.5. This plot summarizes several of the figures shown in the previous chapters, because it is important to note that while the magnitude of the Seebeck coefficient may be dependent on composition (indicated by different symbols), it always peaks when the fluctuations in the Yb valence are maximized. Figure 7-2 provides strong motivation for further investigation of Yb-

based compounds and a means to tailor the thermoelectric properties to optimize the Seebeck coefficient via solid solution alloying. Understanding the underlying physics of this behavior is an outstanding problem and would be an interesting question to investigate in the future.

REFERENCES

REFERENCES

- [1] T. J. Seebeck and A. v (Arthur) Oettingen, *Magnetische Polarisation der Metalle und Erze durch Temperatur-Differenz, 1822-1823. Hrsg. von A.J. v. Oettingen.* Leipzig W. Engelmann, 1895.
- [2] S. Kasap, "Thermoelectric effects in metals: Thermocouples," *Can. Dep. Electr. Eng. Univ. Sask.*, 2001.
- [3] D. T. Morelli, "Thermoelectric Devices," *Encyclopedia of Applied Physics*, vol. 21. WILEY-VCH Verlag GmbH & Co KGaA, 1997.
- [4] T. M. Tritt, "Thermoelectric Materials: Principles, Structure, Properties, and Applications," *Encyclopedia of Materials: Science and Technology*. Elsevier, 2002.
- [5] G. Mahan, B. Sales, and J. Sharp, "Thermoelectric Materials: New Approaches to an Old Problem," *Phys. Today*, vol. 50, no. 3, pp. 42–47, 1997.
- [6] J. Zheng, "Recent advances on thermoelectric materials," *Front. Phys. China*, vol. 3, no. 3, pp. 269–279, Jul. 2008.
- [7] D. M. Rowe, Ed., *Thermoelectrics Handbook: Macro to Nano*, 1st ed. CRC Press, 2005.
- [8] "Thermoelectric Overview," *Noah Precision, LLC*, 2011. [Online]. Available: <http://www.lauda-noah.com/thermoelectric-overview.html>. [Accessed: 14-Oct-2014].
- [9] P. Dyches, "Radioisotope Thermoelectric Generator (RTG)," *Solar System Exploration*. [Online]. Available: <http://solarsystem.nasa.gov/rps/rtg.cfm>. [Accessed: 25-Sep-2014].
- [10] K. Tate, "Nuclear Generators Power NASA Deep Space Probes (Infographic)," *Space.com*. [Online]. Available: <http://www.space.com/13702-nuclear-generators-rtg-power-nasa-planetary-probes-infographic.html>. [Accessed: 25-Sep-2014].
- [11] J. W. Sharp, "Thermoelectric and Energy Conversion Devices," in *Encyclopedia of Condensed Matter Physics*, F. Bassani, G. L. Liedl, and P. Wyder, Eds. Oxford: Elsevier, 2005, pp. 173–180.
- [12] S. B. Riffat and X. Ma, "Thermoelectrics: a review of present and potential applications," *Appl. Therm. Eng.*, vol. 23, no. 8, pp. 913–935, Jun. 2003.
- [13] A. J. Simon, "U.S Energy Flow Chart." Lawrence Livermore National Lab and Department of Energy.
- [14] G. Chen, M. S. Dresselhaus, G. Dresselhaus, J.-P. Fleurial, and T. Caillat, "Recent developments in thermoelectric materials," *Int. Mater. Rev.*, vol. 48, no. 1, pp. 45–66, Feb. 2003.
- [15] F. J. DiSalvo, "Thermoelectric Cooling and Power Generation," *Science*, vol. 285, no. 5428, pp. 703–706, Jul. 1999.
- [16] L. Laird, "Could TEG Improve Your Car's Efficiency?," *Energy.gov*, 16-Aug-2010. [Online]. Available: <http://energy.gov/articles/could-teg-improve-your-cars-efficiency>. [Accessed: 25-Sep-2014].
- [17] "Alphabet Energy Introduces The World's Most Powerful Thermoelectric Generator," *Alphabet Energy*. [Online]. Available: <http://www.alphabetenergy.com/press-releases/alphabet-energy-introduces-worlds-powerful-thermoelectric-generator/>. [Accessed: 09-Oct-2014].
- [18] R. E. Simons and R. C. Chu, "Application of thermoelectric cooling to electronic equipment: a review and analysis," in *Sixteenth Annual IEEE Semiconductor Thermal Measurement and Management Symposium, 2000*, 2000, pp. 1–9.

- [19] L. Yershova, V. Volodin, T. Gromov, D. Kondratiev, G. Gromov, S. Lamartinie, J. P. Bibring, and A. Soufflot, "Thermoelectric Cooling for Low Temperature Space Environment," in *Proceedings of the 7th European Workshop on Thermoelectrics, Pamplona*, 2002.
- [20] T. M. Davis, J. Reilly, and F. L. B. J. Tomlinson, "Air Force Research Laboratory Cryocooler Technology Development," in *Cryocoolers 10*, R. G. R. Jr, Ed. Springer US, 2002, pp. 21–32.
- [21] G. J. Snyder and E. S. Toberer, "Complex thermoelectric materials," *Nat. Mater.*, vol. 7, no. 2, pp. 105–114, Feb. 2008.
- [22] H. J. Goldsmid and R. W. Douglas, "The use of semiconductors in thermoelectric refrigeration," *Br. J. Appl. Phys.*, vol. 5, no. 11, p. 386, Nov. 1954.
- [23] G. D. Mahan and J. O. Sofo, "The best thermoelectric," *Proc. Natl. Acad. Sci.*, vol. 93, no. 15, pp. 7436–7439, Jul. 1996.
- [24] A. F. Ioffe, "On thermal conduction in semiconductors," *Il Nuovo Cimento Ser. 10*, vol. 3, no. 4, pp. 702–715, Apr. 1956.
- [25] A. V. Ioffe and A. F. Ioffe, "Thermal conductivity of semiconductor solid solutions," *Sov. Phys. Solid State*, vol. 2, pp. 719–728, 1960.
- [26] R. Berman, *Thermal Conduction in Solids*. Oxford: Oxford University Press, 1976.
- [27] P. G. Klemens, "Thermal Resistance due to Point Defects at High Temperatures," *Phys. Rev.*, vol. 119, no. 2, pp. 507–509, Jul. 1960.
- [28] C. Suryanarayana, "Mechanical alloying and milling," *Prog. Mater. Sci.*, vol. 46, no. 1–2, pp. 1–184, Jan. 2001.
- [29] Z. A. Munir, U. Anselmi-Tamburini, and M. Ohyanagi, "The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method," *J. Mater. Sci.*, vol. 41, no. 3, pp. 763–777, Feb. 2006.
- [30] M. Omori, "Sintering, consolidation, reaction and crystal growth by the spark plasma system (SPS)," *Mater. Sci. Eng. A*, vol. 287, no. 2, pp. 183–188, Aug. 2000.
- [31] H. J. Goldsmid and A. W. Penn, "Boundary scattering of phonons in solid solutions," *Phys. Lett. A*, vol. 27, no. 8, pp. 523–524, Sep. 1968.
- [32] S. Kasap, "Chapter 5: Semiconductors," in *Principles of Electronic Materials and Devices*, 3 edition., Boston: McGraw-Hill Science/Engineering/Math, 2005.
- [33] N. Oeschler, S. Hartmann, U. Köhler, M. Deppe, P. Sun, and F. Steglich, "Thermoelectric Power of Correlated Compounds," in *Properties and Applications of Thermoelectric Materials*, V. Zlatić and A. C. Hewson, Eds. Springer Netherlands, 2009, pp. 81–90.
- [34] V. Zlatić and R. Monnier, "Theory of the thermoelectricity of intermetallic compounds with Ce or Yb ions," *Phys. Rev. B*, vol. 71, no. 16, Apr. 2005.
- [35] M. B. Maple, L. E. DeLong, and B. C. Sales, "Chapter 11 Kondo effect: Alloys and compounds," in *Handbook on the Physics and Chemistry of Rare Earths*, vol. Volume 1, J. and L. E. Karl A. Gschneidner, Ed. Elsevier, 1978, pp. 797–846.
- [36] M. D. Daybell and W. A. Steyert, "Localized Magnetic Impurity States In Metals: Some Experimental Relationships," *Rev. Mod. Phys.*, vol. 40, no. 2, pp. 380–389, Apr. 1968.
- [37] B. Batlogg, E. Kaldis, and P. Wachter, "Mixed valence compounds with hopping conductivity," *J. Magn. Magn. Mater.*, vol. 3, no. 1–2, pp. 96–98, Mar. 1976.
- [38] E. Kaldis, A. Schlegel, P. Wachter, and C. Zurcher, "Electronic structure of divalent-, trivalent- and mixed valence rare earth compounds," *J. Magn. Magn. Mater.*, vol. 3, no. 1–2, pp. 1–3, Mar. 1976.

- [39] J. M. Lawrence, P. S. Riseborough, and R. D. Parks, "Valence fluctuation phenomena," *Rep. Prog. Phys.*, vol. 44, no. 1, p. 1, Jan. 1981.
- [40] B. C. Sales and D. K. Wohlleben, "Susceptibility of Interconfiguration-Fluctuation Compounds," *Phys. Rev. Lett.*, vol. 35, no. 18, pp. 1240–1244, Nov. 1975.
- [41] L. L. Hirst, "Theory of magnetic impurities in metals," *Phys. Kondens. Mater.*, vol. 11, no. 3, pp. 255–278, 1970.
- [42] L. L. Hirst, "The configuration-based approach to magnetic impurities in metals," in *AIP Conference Proceedings*, 1975, vol. 24, pp. 11–15.
- [43] E. Colombier, D. Braithwaite, G. Lapertot, B. Salce, and G. Knebel, "High-pressure transport and microcalorimetry studies on high quality $\text{YbCu}_{1/2}\text{Si}_{1/2}$ single crystals," *Phys. Rev. B*, vol. 79, no. 24, p. 245113, Jun. 2009.
- [44] K. Alami-Yadri, H. Wilhelm, and D. Jaccard, "Pressure-induced magnetically ordered Kondo lattice state in YbCu_2Si_2 ," *Eur. Phys. J. B - Condens. Matter Complex Syst.*, vol. 6, no. 1, pp. 5–11, Nov. 1998.
- [45] H. Nowatari, Y. Saiga, Y. Kato, K. Iwata, S. Katano, T. Fujiwara, Y. Uwatoko, and M. Kosaka, "Effect of Pressure on the Electrical Resistivity of YbAl_2 ," *J. Phys. Soc. Jpn.*, vol. 76SA, no. Supplement A, pp. 80–81, 2007.
- [46] C. Dallera, E. Annese, J.-P. Rueff, A. Palenzona, G. Vankó, L. Braicovich, A. Shukla, and M. Grioni, "Valence changes in YbAl_2 under pressure: a resonant inelastic X-ray emission study," *J. Electron Spectrosc. Relat. Phenom.*, vol. 137–140, pp. 651–655, Jul. 2004.
- [47] A. Grytsiv, D. Kaczorowski, V. H. Tran, A. Leithe-Jasper, and P. Rogl, "Crystal structure and physical properties of Yb-based intermetallics $\text{Yb}(\text{Cu}, \text{Ag})_2(\text{Si}, \text{Ge})_2$, $\text{Yb}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{Si}_2$ ($x = 0.65, 0.77$) and $\text{Yb}(\text{Ag}_{0.18}\text{Si}_{0.82})_2$," *J. Alloys Compd.*, vol. 504, pp. 1–6, 2010.
- [48] M. M. A.-E. H. Winkelmann, "Direct observation of a magnetically ordered state in $\text{YbCu}_{1/2}\text{Si}_{1/2}$ under high pressure," *Phys Rev B*, vol. 60, no. 5, 1999.
- [49] M. Sancrotti, I. Abbati, E. Puppini, Z. X. Shen, I. Lindau, R. Eggenhöfner, A. Iandelli, and G. L. Olcese, "Yb mean valence in chemically compressed $\text{Yb}_{1-x}\text{Sc}_x\text{Al}_2$ pseudobinary alloys: An X-ray absorption spectroscopy investigation," *Solid State Commun.*, vol. 74, no. 10, pp. 1131–1135, Jun. 1990.
- [50] L. Braicovich, B. De Michelis, A. Fasana, E. Puppini, M. Sancrotti, E. Vescovo, R. Eggenhöfner, A. Iandelli, G. L. Olcese, and A. Palenzona, "Chemical substitution effect on Yb valence in the surface region of $\text{Yb}_{1-x}\text{M}_x\text{Al}_2$ ($= \text{Sc}, \text{Ca}$): A photoemission investigation," *Solid State Commun.*, vol. 79, no. 1, pp. 75–79, Jul. 1991.
- [51] I. Abbati, B. De Michelis, A. Fasana, M. Sancrotti, A. Iandelli, G. L. Olcese, and R. Eggenhöfner, "Chemical pressure effects and valence fluctuations in $\text{Yb}_{0.6}\text{Ca}_{0.4}\text{Al}_2$ and YbAl_2 alloys: A photoemission investigation," *Solid State Commun.*, vol. 65, no. 7, pp. 743–747, Feb. 1988.
- [52] R. Eggenhöfner, M. Sancrotti, I. Abbati, E. Puppini, Z. X. Shen, I. Lindau, A. Iandelli, and G. L. Olcese, "Yb valence in $\text{Yb}_{1-x}\text{Ca}_x\text{Al}_2$ pseudobinary alloys via Yb LIII X-ray absorption spectroscopy," *Solid State Commun.*, vol. 74, no. 9, pp. 1009–1012, Jun. 1990.
- [53] R. Eggenhöfner and G. L. Olcese, "Chemical pressure behaviour of intermediate valent compounds in the resonance fermi liquid model," *J. Common Met.*, vol. 154, no. 1, pp. 89–98, Oct. 1989.

- [54] K. Alami-Yadri, D. Jaccard, and D. Andreica, "Thermopower of Yb Heavy Fermion Compounds at High Pressure," *J. Low Temp. Phys.*, vol. 114, no. 1–2, pp. 135–149, Jan. 1999.
- [55] B. C. Sales and R. Viswanathan, "Demagnetization due to interconfiguration fluctuations in the RE-Cu₂Si₂ compounds," *J. Low Temp. Phys.*, vol. 23, no. 3–4, pp. 449–467, May 1976.
- [56] B. C. Sales, "A model for the thermodynamic properties of metallic rare earth systems with an unstable valence," *J. Low Temp. Phys.*, vol. 28, no. 1–2, pp. 107–127, Jul. 1977.
- [57] A. Iandelli and G. L. Olcese, "Structural and magnetic investigations on some RAl₂-MAI₂ laves phase systems," *J. Common Met.*, vol. 111, no. 1–2, pp. 145–156, Sep. 1985.
- [58] B. Coqblin, B. Chevalier, and V. Zlatić, "Thermoelectric Power and Thermal Transport of Anomalous Rare-Earth Kondo Compounds," in *Properties and Applications of Thermoelectric Materials*, V. Zlatić and A. C. Hewson, Eds. Dordrecht: Springer Netherlands, 2009, pp. 91–117.
- [59] J. Flouquet and H. Harima, "Heavy fermion material: Ce versus Yb case," arXiv e-print 0910.3110, Oct. 2009.
- [60] V. Zlatić, B. Horvatić, I. Milat, B. Coqblin, G. Czycholl, and C. Grenzebach, "Thermoelectric power of cerium and ytterbium intermetallics," *Phys. Rev. B*, vol. 68, no. 10, pp. 1–11, Sep. 2003.
- [61] P. C. Canfield and Z. Fisk, "Growth of single crystals from metallic fluxes," *Philos. Mag. Part B*, vol. 65, no. 6, pp. 1117–1123, Jun. 1992.
- [62] P. C. Canfield, "Solution Growth of Intermetallic Single Crystals: A Beginner's Guide," *Prop. Appl. Complex Intermet.*, pp. 93–111, 2010.
- [63] N. A. Lange and J. A. Dean, *Lange's handbook of chemistry*, 10th ed. [New York: McGraw-Hill, 1967.
- [64] D. M. Rowe, G. Min, and L. Kuznestsov, "Electrical resistivity and Seebeck coefficient of hot-pressed YbAl₃ over the temperature range 150-700K," *Philos. Mag. Lett.*, vol. 77, no. 2, pp. 105–108, Feb. 1998.
- [65] D. M. Rowe, V. L. Kuznetsov, L. A. Kuznetsova, and G. Min, "Electrical and thermal transport properties of intermediate-valence YbAl₃," *J. Phys. Appl. Phys.*, vol. 35, no. 17, pp. 2183–2186, Sep. 2002.
- [66] G. Min and D. M. Rowe, "A novel thermoelectric converter employing Fermi gas/liquid interfaces," *J. Phys. Appl. Phys.*, vol. 32, no. 6, p. L26, Mar. 1999.
- [67] T. He, T. G. Calvarese, J.-Z. Chen, H. D. Rosenfeld, R. J. Small, J. J. Krajewski, and M. A. Subramanian, "Origin of low thermal conductivity in α -Mn: enhancing the ZT of YbAl₃ and CoSb₃ through Mn addition," in *24th International Conference on Thermoelectrics, 2005. ICT 2005*, 2005, pp. 434 – 439.
- [68] S. Ohara, G. F. Chen, and I. Sakamoto, "Effect of pressure on transport properties of mixed-valence compound YbAl₃," *J. Alloys Compd.*, vol. 323–324, pp. 632–635, Jul. 2001.
- [69] C. L. Foiles, "Thermopower of GdIn₃ and YbAl₃," *J. Appl. Phys.*, vol. 52, no. 3, pp. 2217–2219, Mar. 1981.
- [70] J. Zhou, Z. Sun, X. Cheng, and Y. Zhang, "Phase stability and electronic structures of YbAl₃-xM_x (M=Mg, Cu, Zn, In and Sn) studied by first-principles calculations," *Intermetallics*, vol. 17, no. 12, pp. 995–999, Dec. 2009.
- [71] J. Zhou, B. Sa, and Z. Sun, "First-principles investigations on phase stability and electronic structures of Yb_{1-x}M_xAl₃ (M = Ho, Er and Tm) alloys," *Intermetallics*, vol. 18, no. 12, pp. 2394–2398, Dec. 2010.

- [72] R. E. Majewski, A. S. Edelstein, A. T. Aldred, and A. E. Dwight, "Susceptibility measurements on the valence fluctuation system (Yb,Sc)Al₃," *J. Appl. Phys.*, vol. 49, no. 3, pp. 2096–2097, Mar. 1978.
- [73] S. Lee, J. Park, P. Canfield, and D. Lynch, "Optical properties and electronic structures of single crystalline RAl₃ (R=Sc, Yb, and Lu)," *Phys. Rev. B*, vol. 67, no. 7, Feb. 2003.
- [74] E. D. Bauer, C. H. Booth, J. M. Lawrence, M. F. Hundley, J. L. Sarrao, J. D. Thompson, P. S. Riseborough, and T. Ebihara, "Anderson lattice behavior in Yb_{1-x}Lu_xAl₃," *Phys. Rev. B*, vol. 69, no. 12, p. 125102, Mar. 2004.
- [75] G. J. Lehr and D. T. Morelli, "Synthesis, crystal structure, and thermoelectric properties of the YbAl₃-ScAl₃ solid solution," *Intermetallics*, vol. 32, no. 0, pp. 225–229, Jan. 2013.
- [76] G. J. Lehr and D. T. Morelli, "Thermoelectric Properties of Yb_{1-x}(Er,Lu)_xAl₃ Solid Solutions," *J. Electron. Mater.*, vol. 42, no. 7, pp. 1697–1701, Jul. 2013.
- [77] J. L. Moriarty, J. E. Humphreys, R. O. Gordon, and N. C. Baenziger, "X-ray examination of some rare-earth-containing binary alloy systems," *Acta Crystallogr.*, vol. 21, no. 5, pp. 840–841, Nov. 1966.
- [78] F. G. Meng, L. G. Zhang, H. S. Liu, L. B. Liu, and Z. P. Jin, "Thermodynamic optimization of the Al–Yb binary system," *J. Alloys Compd.*, vol. 452, no. 2, pp. 279–282, Mar. 2008.
- [79] K. A. Gschneidner and F. W. Calderwood, "The Al–Yb (Aluminum–Ytterbium) system," *Bull. Alloy Phase Diagr.*, vol. 10, no. 1, pp. 47–49, Feb. 1989.
- [80] Y. Harada and D. . Dunand, "Microstructure of Al₃Sc with ternary transition-metal additions," *Mater. Sci. Eng. A*, vol. 329–331, no. 0, pp. 686–695, Jun. 2002.
- [81] T. P. Braun and F. J. DiSalvo, "Transport properties of intermetallic thulium compounds," *J. Alloys Compd.*, vol. 305, no. 1–2, pp. 43–48, Jun. 2000.
- [82] A. Hiess, J. X. Boucherle, F. Givord, J. Schweizer, E. Lelièvre-Berna, F. Tasset, B. Gillon, and P. C. Canfield, "Magnetism in intermediate-valence YbAl₃ : a polarized neutron diffraction study," *J. Phys. Condens. Matter*, vol. 12, no. 6, pp. 829–840, Feb. 2000.
- [83] D. M. Rowe, G. Min, and V. L. Kuznetsov, "Thermoelectric properties of hot-pressed YbAl₃ compound over temperature range 150–800 K," in *XVI International Conference on Thermoelectrics, 1997. Proceedings ICT '97*, 1997, pp. 528–531.
- [84] J. Murray, "The Al–Sc (aluminum–scandium) system," *J. Phase Equilibria*, vol. 19, no. 4, pp. 380–384, 1998.
- [85] K. A. Gschneidner and F. W. Calderwood, "The Al–Er (Aluminum–Erbium) system," *Bull. Alloy Phase Diagr.*, vol. 9, no. 6, pp. 676–678, Dec. 1988.
- [86] H. Okamoto, "Al–Lu (aluminum–lutetium)," *J. Phase Equilibria*, vol. 14, no. 3, pp. 394–395, Jun. 1993.
- [87] S. J. Lee, S. Y. Hong, I. R. Fisher, P. C. Canfield, B. N. Harmon, and D. W. Lynch, "Optical properties and electronic structure of single crystals of LuAl₂ and YbAl₂," *Phys. Rev. B*, vol. 61, no. 15, pp. 10076–10083, Apr. 2000.
- [88] T. Görlach, C. Pfleiderer, K. Grube, and H. v. Löhneysen, "Low-temperature properties of YbAl₂," *Phys. Rev. B*, vol. 71, no. 3, p. 033101, Jan. 2005.
- [89] G. J. Lehr, D. T. Morelli, H. Jin, and J. P. Heremans, "Enhanced thermoelectric power factor in Yb_{1-x}Sc_xAl₂ alloys using chemical pressure tuning of the Yb valence," *J. Appl. Phys.*, vol. 114, 2013.
- [90] H. J. van Daal, P. B. van Aken, and K. H. J. Buschow, "The seebeck coefficient of YbAl₂ and YbAl₃," *Phys. Lett. A*, vol. 49, no. 3, pp. 246–248, Sep. 1974.

- [91] W. Franz, F. Steglich, W. Zell, D. Wohlleben, and F. Pobell, "Intermediate Valence on Dilute Europium Ions," *Phys. Rev. Lett.*, vol. 45, no. 1, pp. 64–67, Jul. 1980.
- [92] N. D. Dung, T. D. Matsuda, Y. Haga, S. Ikeda, E. Yamamoto, T. Ishikura, T. Endo, S. Tatsuoka, Y. Aoki, H. Sato, T. Takeuchi, R. Settai, H. Harima, and Y. Ōnuki, "de Haas-van Alphen Effect and Fermi Surface Properties in High-Quality Single Crystals YbCu₂Si₂ and YbCu₂Ge₂," *J. Phys. Soc. Jpn.*, vol. 78, no. 8, Aug. 2009.
- [93] B. C. Kuzhel, I. D. Shcherba, and I. I. Kravchenko, "The contribution of valence unstable ytterbium states into kinetic properties of YbNi_{2-x}Ge_{2+x} and YbCu_{2-x}Si_{2+x}," *J. Alloys Compd.*, vol. 425, no. 1–2, pp. 54–58, Nov. 2006.
- [94] D. Andreica, K. Alami-Yadri, D. Jaccard, A. Amato, and A. Schenck, "Transport properties and μ SR spectroscopy of Yb(Ni_xCu_{1-x})₂Si₂," *Phys. B Condens. Matter*, vol. 259–261, pp. 144–145, Jan. 1999.
- [95] K. Alami-Yadri, H. Wilhelm, and D. Jaccard, "Transport properties of Yb-compounds at high pressure," *Phys. B Condens. Matter*, vol. 259–261, pp. 157–158, Jan. 1999.
- [96] E. V. Sampathkumaran, L. C. Gupta, and R. Vijayaraghavan, "NMR studies in ICF systems of RECu₂Si₂ compounds," *J. Phys. C Solid State Phys.*, vol. 12, no. 20, p. 4323, Oct. 1979.
- [97] C. N. R. Rao, D. D. Sarma, P. R. Sarode, E. V. Sampathkumaran, L. C. Gupta, and R. Vijayaraghavan, "Valence fluctuation in some Yb intermetallics by X-ray photoemission and X-ray absorption," *Chem. Phys. Lett.*, vol. 76, no. 3, pp. 413–415, Dec. 1980.
- [98] T. D. Matsuda, N. D. Dung, Y. Haga, S. Ikeda, E. Yamamoto, T. Ishikura, T. Endo, T. Takeuchi, R. Settai, and Y. Ōnuki, "Fermi surface properties of YbCu₂Si₂," *Phys. Status Solidi B*, vol. 247, no. 3, pp. 757–759, 2010.
- [99] T. K. Hatwar, R. M. Nayak, B. D. Padalia, M. N. Ghatikar, E. V. Sampathkumaran, L. C. Gupta, and R. Vijayaraghavan, "X-ray absorption spectroscopic study of mixed valence systems EuCu₂Si₂, YbCu₂Si₂ and Sm₄Bi₃," *Solid State Commun.*, vol. 34, no. 8, pp. 617–620, May 1980.
- [100] G. J. Lehr and D. T. Morelli, "YbCu₂Si₂-LaCu₂Si₂ solid solutions with enhanced thermoelectric power factor," *J. Electron. Mater.*, pending.
- [101] I. L. Spain, F. Steglich, U. Rauchschwalbe, and H. D. Hochheimer, "Energy dispersive in situ high pressure study of stoichiometric and non-stoichiometric rare earth coppersilicides," *Phys. BC*, vol. 139–140, pp. 449–452, May 1986.