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The Thermoelectric Properties Investigation of $X_{0.05}Mo_3Sb_{7-y}Te_y$ ($X=Mn, Fe, Ni, Co; y=1.5, 1.6, 1.7$)

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THE THERMOELECTRIC PROPERTIES
INVESTIGATION OF X_{0.03}Mo_{3}Sb_{7-y}Te_{y}
(X=Mn, Fe, Ni, Co; y=1.5, 1.6, 1.7)

A Thesis
Presented to
the Graduate School of
Clemson University

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

by
Tim C. Holgate
December 2008

Accepted by:
Dr. Terry M. Tritt, Committee Chair
Dr. Jian He
Dr. Fivos Drymiotis
ABSTRACT

With ever increasing energy costs, dwindling resources, and terms with the prefix “green” filling headlines, the need for environmentally friendly energy sources has never been greater. Since the mid-20th century researchers have been pursuing greater efficiency in thermoelectric materials. Thermoelectric materials achieve energy conversion via the Seebeck effect (heat to electric power) and the Peltier effect (electricity to cooling power).

Presented herein are the measured electrical and thermal transport properties and phenomenal analysis of the Ir₃Ge₇-type system: \( X_{0.05}Mo₃Sb₇₋yTe_y \) (\( X=\text{Mn, Fe, Ni, Co} \); \( y=1.5, 1.6, 1.7 \)) where “\( X \)” are interstitially doped metal ions.

First, the effect of the substitution ratio of Te was studied in the Fe subsystem. Te, having one more electron than Sb, decreases carrier concentration as \( Mo₃(Sb,Te)₇ \) has been observed to be p-type. Because of the decrease in the majority charge carrier, it is expected that both the Seebeck coefficient and resistivity will increase with tellurium content.

Holding \( y=1.6 \) and varying the transition metal ion atomic number allowed for an analysis of the effectiveness of the dopants as a means to lower thermal conductivity. A prediction of the effect of dopant atomic number on thermal conductivity is not possible as too many factors come into play, such as bond strength between the dopant and parent matrix and atomic radius of the dopant.
DEDICATION

I dedicate this work to the newest love of my life—my son, Isaac, and to the sweetest love of my life—my wife, Lauren. Finally, I dedicate this work and all others to the greatest Love of my life—Jesus.
ACKNOWLEDGEMENTS

I would first like to thank Dr. Terry Tritt for allowing me to be a member of his wonderful group. I owe a great deal of my wonderful experiences as a graduate student to the wonderful people I work with. Even more so, I would like to thank Dr. Tritt for mentorship, guidance, and friendship.

A special thanks to Dr. Holger Kleinke from the University of Waterloo. Not only has his collaboration made my work on this project an enjoyable experience, it has, in the first place, made it possible.

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Additionally, I would like to thank Zhe Su for all the times he has assisted me in making high temperature resistivity and Seebeck coefficient measurements without any thought of recompense.
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INTRODUCTION

Thermoelectrics

The search for clean and renewable energy sources continues to intensify as the world’s population grows and traditional, nonrenewable resources are consumed. Energy conversion between thermal and electrical types is achieved through the Seebeck and Peltier effects in the form of power generation and thermoelectric cooling, respectively. Materials that exhibit this cross-transport phenomenon are known as thermoelectric materials.

Transport Mechanisms

It is observed that many natural laws take the form of an action being proportional to a result. In this formulation the “constant” of proportionality describes the system, and is often a function of some other system variable, such as temperature. An example of this would be Newton’s Second Law, $F=ma$, where $F$ is a force acting on a system of mass, $m$, which in turn experiences an acceleration, $a$. Of course in the aforementioned example mass is truly a constant. Additionally, and without consequence, the relationship can be inversely expressed as $a=F/m$. This follows logical flow more closely as a result equaling a force acting on a “system.”

Where two or more actions have the potential to act upon a system, the necessary formulation takes on the form of a tensor with cross-terms relating each action with
results that are naturally associated with each of the other actions. For example, consider a system influenced by two acting forces—an electric field and a thermal gradient. The natural responses of the system would be a flux of charge \(J_e\) and of heat \(J_h\), respectively.

\[
\begin{align*}
\vec{J}_e &= \sigma \vec{E} \\
\vec{J}_h &= \kappa \vec{\nabla}T / T
\end{align*}
\]

(1.1) (1.2)

Each flux, however, is a linear combination of both motivations. In tensor form this is expressed as

\[
\begin{pmatrix}
\vec{J}_e \\
\vec{J}_h
\end{pmatrix} =
\begin{pmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{pmatrix}
\begin{pmatrix}
\vec{E} \\
\vec{\nabla}T / T
\end{pmatrix}
\]

(1.3)

with \(L_{11} = \sigma\) and \(L_{22} = \kappa\), the electrical and thermal conductivities. This formulation follows Onsager’s relation, which states \(L_{12} = L_{21}\) for all irreversible transport properties.[1] These cross terms are the very essence of thermoelectricity and are closely related to the Seebeck and Peltier coefficients. These quantities can be arrived at by \(\vec{V}T\) and \(J_e = 0\) for the Seebeck and \(\vec{V}T = 0\) for the Peltier while neglecting Joule and Thompson heating.[2]
Seebeck Effect

Named after Thomas Johann Seebeck, who discovered the phenomenon in 1821,[3] the Seebeck Effect is the resulting voltage difference between two ends of a metallic bar to which a temperature gradient is applied. The temperature gradient of the material is transferred to the electrons in the conducting band. This causes a non-equilibrium condition in terms of energies of the conducting electrons, which can be thought of as a Fermi gas.[4] The electrons will diffuse from the hot to the cold side of the material according to the Second Law of Thermodynamics, seeking equilibrium of total thermal energy. This motivation to diffuse can be thought of as a chemical potential.[5] Electrons at the hot side (actually just “hotter” since “hot” and “cold” are relative terms) will continue to diffuse until the Coulomb potential of the already diffused electrons balances this chemical potential. The non-uniform charge distribution will result in an electric field proportional to the temperature gradient. Between two points on the material, the proportionality factor, or the Seebeck coefficient, $a$, relates the potential difference, $\Delta V$, to the difference in temperature, $\Delta T$, in the following equation:

$$\Delta V = -a \Delta T$$ (1.4)

The Seebeck effect can also be observed in a simple circuit loop made of two different metals (A, B) with a voltmeter in the middle of one of them (Fig. 1.1). Holding the junctions at different temperatures induces a temperature gradient in both conductors. The overall temperature difference across each conductor is obviously the same. If both conductors have the same charge carrier species their individual e.m.f.’s will oppose each
other and the result will be the difference. From this the relative Seebeck coefficient can be determined.[6]

\[
\alpha_{AB} = -\frac{V_{AB}}{\Delta T} = \alpha_A - \alpha_B
\]  

(1.5)

**Peltier Effect**

Closely related to the Seebeck effect is the Peltier Effect. Heat is observed to be continuously added or subtracted when current is passed through a junction of dissimilar metals (Fig. 1.2). This is due to the difference in energy of the Fermi levels, \( \varepsilon_F \), of the two conductors. As an electron passes from a metal of a lower \( \varepsilon_F \) to that of a higher \( \varepsilon_F \), the electron must absorb heat energy to make the step. This is Peltier cooling as the heat absorbed was taken from the junction. Alternatively, when electrons are transferred from a material of higher \( \varepsilon_F \) to that of a lower \( \varepsilon_F \), heat is expelled to the junction as the electron steps down in energy.

The Peltier coefficient, \( \Pi \), relates the rate of transfer of heat expelled or absorbed, \( \frac{dQ}{dt} \), to the current, \( J \), passing through the junction of metals \( a \) and \( b \). Through the Thomson relations it is also equal to the Seebeck coefficient scaled by the temperature, \( T \).[2]

\[
\frac{dQ_{ab}}{dt} = \Pi_{ab}J = \alpha TJ
\]  

(1.6)
Thomson Effect

When current is passed through a uniform conductor of a constant cross-section is held at a constant temperature gradient, heat must be supplied in order to maintain the temperature gradient. The sign of the heat transfer is determined by both the direction of the current relative to the direction of the temperature gradient and the material. The Thomson coefficient, $\beta$, relates the heat production per a unit volume, $q$, to the current density, $J$, and the temperature gradient, $\Delta T$.

$$q = \rho J^2 - \beta J \Delta T$$  \hspace{1cm} (1.7)

The first term is the Joule heating, which is equal to the resistivity, $\rho$, times the square of the current density. The second term is the Thomson heat, which changes sign with $J$. 

Figure 1.1 Seebeck Effect
Figure 1.2 Peltier Effect

Heat expelled or absorbed depending on direction of I
Sample Characterization

Good thermoelectric materials will generally exhibit a high Seebeck coefficient—thermopower, alternatively—along with low electrical resistivity and low thermal conductivity. As these transport properties are inherently codependent on other properties, such as density and carrier concentration, decoupling and optimizing them is not a simple task. The most common route to optimizing a thermoelectric material is to target lowering the thermal conductivity while optimizing the thermopower and resistivity. Typically, metals exhibit a low thermopower and low resistivity while semiconductors usually have a high thermopower and high resistivity.

Seebeck Coefficient

Previously we defined the Seebeck coefficient as the proportionality constant between a $\Delta V$ and the $\Delta T$ that produced it. This, of course, is an oversimplified view of the phenomenon. The Seebeck coefficient is actually a function of temperature and a tensor, and therefore Eq. 1.4 is only locally, or infinitesimally, defined. When measuring the Seebeck coefficient of a bulk sample the infinitesimal $\Delta V$'s and $\Delta T$'s are summed up over the entire sample by measuring the total $\Delta V_{\text{tot}}$ and $\Delta T_{\text{tot}}$ between the ends. This gives an average $\alpha(T_{\text{avg}})$ where $T_{\text{avg}}$ is defined as $T_{\text{cold}} + \frac{1}{2}\Delta T_{\text{tot}}$. 
Resistivity

The ease with which electrical current travels through a sample is very important to thermoelectric performance. This characterization is quantified as resistivity. Macroscopically, resistivity, $\rho$, is defined as the resistance, $R$, per unit length, $l$, multiplied by the cross-sectional area of the material, $A$.

$$\rho = \frac{RA}{l}$$

(1.8)

The electrical conductivity, $\sigma$, is simply the inverse of the resistivity.

$$\sigma = \frac{1}{\rho}$$

(1.9)

Hall Coefficient

Charged particles moving in a magnetic field experience the Lorentz force, which acts on the particle in a direction perpendicular to the plane in which the velocity vector of the particle and magnetic field vector lie.[7] The magnitude of this force is the cross product of the velocity and magnetic field vectors, scaled by the magnitude of the charge.

$$\vec{F} = q\vec{v} \times \vec{B}$$

(1.10)

When an electric current is passing through a conductor placed in an external magnetic field, the Lorentz force induces a charge distribution along the direction of the
force. Once the Lorentz force is balanced by the Coulomb force due to the electric field of the charge distribution, a potential difference across the conductor can be measured. Known as the Hall voltage, it is proportional to the magnitude of the electrical current, $I$, and the magnetic field, $B$ (Fig. 1.3). In a metal that only has one type of charge carrier the Hall voltage is expressed as

$$V_H = -\frac{IB}{dne}$$  \hspace{1cm} (1.11)

where $n$ is the charge carrier concentration, $e$ is the charge of the carrier, and $d$ is the thickness of the conductor along the direction of the magnetic field. A system can be intrinsically described by its Hall coefficient, which is defined as

$$R_H = \frac{-1}{ne}$$  \hspace{1cm} (1.12)

The Hall coefficient is slightly more complicated for semiconductors where both carriers (electrons and holes) are present. The carrier mobilities of each carrier species weights the Hall coefficient, which for a low to moderate strength magnetic field is represented by

$$R_H = \frac{-n\mu_e^2 + p\mu_h^2}{e(n\mu_e + p\mu_h)^2}$$  \hspace{1cm} (1.13)

with $\mu_e, h$ being the carrier mobility and $n$ and $p$ the electron and hole concentrations.[8]

In high magnetic fields, the Hall coefficient reduces to
Thermal Conductivity

Heat transport is another important property of thermoelectric materials. Since thermoelectric voltage is proportional to $\Delta T$, samples with poor thermal conductivity, $\kappa$, can be expected to perform better than those of high $\kappa$. If a material has an infinitely high $\kappa$ value, it will be impossible to achieve a temperature gradient.

Heat is transported by two mechanisms: phonons, or lattice vibrations, and by thermalized electrons in the conduction band. Each mechanism contributes to the total thermal conductivity independently as seen in the following equation:

$$\kappa_{tot} = \kappa_p + \kappa_e$$  \hspace{1cm} (1.15)

Thermal conductivity is limited by four main types of scattering: phonon-phonon, electron-phonon, boundary, and impurity scattering of both electrons and phonons. Electron-electron scattering is also possible but weakly contributes to electrical and thermal conductivity because of constraints imposed by the Pauli Exclusion Principle.[9] Since only electrons in the conduction band participate in thermal transport, the electron contribution to the thermal conductivity, $\kappa_e$, is directly related to the electrical conductivity, $\sigma$, through the Wiedemann-Franz relation:

$$\kappa_e = \sigma L_e T$$  \hspace{1cm} (1.16)
where \( T \) is the absolute temperature and \( L_0 \) is the Lorentz number: \( 2.44 \times 10^8 \, V^2 K^{-2} \).[10]

In metals, the phonon contribution is influenced most by two processes: phonon-electron scattering and a particular form of phonon-phonon scattering named Umklapp scattering. Umklapp scattering occurs when two phonons of relativity high momentum interact and create a third phonon with a momentum vector larger than the 1st Brillouin Zone, which is the unit cell in momentum space. Quantum mechanically the resulting phonon is unallowable. This results in a quantum of energy being transferred to the lattice and the created phonon being of less momentum than the sum of the incident two and directed backwards—thus the name Umklapp, which means “folded” in German. Umklapp scattering does not conserve total phonon momentum and therefore restricts the flow of heat. This type of scattering dominates at high temperatures while at low temperatures phonon-electron scattering holds the most influence.[9]

**Heat Capacity and Specific Heat**

Heat capacity is defined as the ratio of the amount of heat input to the magnitude of the resulting temperature change. Not all of the heat necessarily is attributed to raising the temperature of the sample. It is possible that the heat is converted to other types of work. Examples of such work include the material undergoing thermal expansion or a phase transition. The heat input term becomes the change in internal energy of the system, \( U \), plus the work done on the system, \( W \).
When a system is held at a constant volume no compression-expansion work is done. Within the temperature range where no phase transition occurs, all the heat input works to raise the internal energy of the system. Therefore, heat capacity at a constant volume, $C_V$, is defined as the rate of change in the internal energy with respect to temperature.

$$C_V = \frac{\partial U}{\partial T}$$  \hspace{1cm} (1.18)

Because it is considerably easier, it is more common to measure heat capacity at a constant pressure, $C_p$. Here compression-expansion work is done and the work term, $W$, in $dU$ is no longer zero. Expanding $dU$ results in $TdS - pdV$ where $T$ is the temperature, $S$ is the entropy, $p$ is the pressure and $V$ is the volume. When this is substituted into $dQ$, and considering $dW$ for compression-expansion work only becomes $pdV + Vdp$, which for a constant pressure reduces to $pdV$, the numerator of the heat capacity is simply $TdS$. In the case of constant pressure this is the differential of the enthalpy, $H$. This leads to the defining of the heat capacity at a constant pressure as the change in enthalpy with respect to temperature.

$$C_p = \frac{\partial H}{\partial T}$$  \hspace{1cm} (1.19)
So far only an extensive quantity has been defined, which depends on the size of the system. It is more useful to define the intensive quantity specific heat capacity, \( c_p \) or \( c_v \), which is defined as heat capacity per a unit mass (or molar mass).

\[
c_{p,v} = \frac{C_{P,V}}{m}
\]  

(1.20)

There is a connection between \( c_p \) and \( c_v \) shown through the following relation:

\[
c_p - c_v = \frac{\alpha_T^2 T}{\rho \beta_T}
\]  

(1.21)

Here \( \alpha_T \) is the thermal expansion coefficient, \( \rho \) is the density, and \( \beta_T \) is the isothermal compressibility, all at temperature \( T \).[11]

In 1819 French scientist Dulong and Petit published a paper stating that “atoms of all simple bodies have exactly the same [heat capacity].”[12] This model in its modern form states that the heat capacity of a solid is equal to three times the product of the universal gas constant, \( R \), and the number of moles of atoms. This, however, only models \( C_V \) at temperatures well above room temperature. It is therefore known as Dulong-Petit Limit of \( C_V \).

\[
C_{V,T \geq 300K} \rightarrow 3nR
\]  

(1.22)

At low temperatures, where the Dulong-Petit model fails, the Debye model nicely describes the heat capacity. Debye’s model involved a \( T^3 \) behavior describing the lattice
thermal conductivity at low temperatures as well as a linear term from the electronic 
contribution in metals.\[13\] The total heat capacity is therefore

\[ C_v = \frac{\pi^2 N k_B^2}{2 \varepsilon_F} T + \frac{12 \pi^4 N k_B}{5 \theta_D^3} T^3 \]  

(1.23)

where \( N \) is the number of atoms, \( k_B \) is the Boltzmann constant, \( \varepsilon_F \) is the Fermi energy, and \( \theta_D \) is the Debye temperature, which is a collection of constants involving the speed of sound in the material, \( c_s \), Planck’s constant, \( h \), as well as \( k_B, N \), and the volume, \( V \).

\[ \theta_D = \frac{h c_s}{2 k_B} \left( \frac{6 N}{\pi V} \right)^{\frac{1}{3}} \]  

(1.24)

By fitting the \( c_p \) data below 5K to Eq. 1.23 we can determine the Debye temperature of the system. It is most convenient to plot specific \( C_P/T \) versus \( T^2 \) and apply a linear fit. Finally, the Debye temperature can be estimated using Eq. 1.27 where \( n \) is the number of moles, and \( a \) the number of atoms per molecule.

\[ \frac{C_P}{T} = \gamma + \beta T^2 \]  

(1.25)

\[ \theta_D = \left( \frac{12}{5} \pi^4 N k_B \right)^{\frac{1}{3}} \left( \frac{3.2277 \times 10^{-21} N}{\beta} \right)^{\frac{1}{3}} \]  

(1.26)

\[ \theta_D = \left( \frac{1943.77 \cdot n \cdot a}{\beta} \right)^{\frac{1}{3}} \]  

(1.27)
Of course, measuring specific heat capacity in units of Jmol$^{-1}$K$^{-1}$ and fitting the data with Eq. 1.25 will lead to calculating $\theta_D$ with Eq. 1.28.

\[
\theta_D \approx \left( \frac{1943.77a}{\beta} \right)^{1/3}
\]

(1.28)
Power Factor

The power factor of a material describes its electronic contribution to its overall efficiency as a thermoelectric material. Consisting of the Seebeck coefficient and electrical conductivity at a temperature $T$, the power factor is given by

$$p.f. = \alpha^2 \sigma T$$

(1.29)

Both $\alpha$ and $\sigma$ depend on carrier concentration and therefore the power factor also exhibits a strong dependence on the carrier concentration. The power factor as a function of carrier concentration is typically maximized around $10^{19}/\text{cm}^3$, which corresponds to a semiconductor (Fig. 1.4).

Figure-of-Merit

The overall efficiency of a thermoelectric material takes into consideration both the electrical and thermal transport properties. This dimensionless figure-of-merit, or $ZT$, is the power factor divided by the total thermal conductivity. From Eq. 1.30 it can be seen that $ZT$ is optimized by a high thermopower, low electrical resistivity, and low thermal conductivity.

$$ZT = \frac{\alpha^2 \sigma T}{\kappa_{\text{tot}}}$$

(1.30)

Current high $ZT$ materials include both p and n-type Bi$_2$Te$_3$. Both having a maximum $ZT$ near 1 at about 100°C, they are industry standards in thermoelectric
cooling devices. At higher temperatures, both p and n-type PbTe are industry standards for thermoelectric power generation with ZT’s of 0.8 and 0.7 in the area of 400°C for n-type and p-type, respectively. Additionally, the p-type TAGS (Tellurium-Antimony-Germanium-Silver) materials have been found to exhibit a high ZT approaching a ZT of 1.2 in the same region as PbTe.[14]

As a direct result of the electronic contribution to the thermal conductivity being proportional to the electrical conductivity, and thus dependent on carrier concentration, the ZT is maximized at a particular carrier concentration corresponding to a doped semiconductor with a small band gap.
Fig. 1.3 Hall Effect
Fig. 1.4 Power Factor as a Function of Carrier Concentration
Material Introduction

The Ir\(_3\)Ge\(_7\) structure consists of an Ir cation surrounded by eight Ge anions in the form of a square antiprism. Direct Ir-Ir bonding leads to a second antiprism, with the two sharing a face where four coplanar Ge atoms are arranged in a square (Fig. 1.5a). This substructure is bonded to identical neighbors via Ge-Ge bonds. This leads to infinite linear chains where each Ir\(_2\)Ge\(_{12}\) double antiprism is separated by a Ge\(_8\) cage along the direction of the chain. In three dimensions these linear chains are formed along all three axes and intersect at the Ge\(_8\) cubes, where the corners of the unit cell are located. The unit cell corners are located in the middle of the Ge\(_8\) cubes (Fig. 1.5b).[15]

Mo\(_3\)Sb\(_7\) is isostructural to Ir\(_3\)Ge\(_7\). By substitution of Te at Sb sites the material may be rendered semiconducting. This along with the high symmetry and presence of Sb\(_8\) cages for use as phonon scattering dopant sites makes Mo\(_3\)Sb\(_7\) a candidate for thermoelectrics. Density of states (DOS) calculations were performed at the University of Waterloo by Dr. Kleinke’s group for Mo\(_3\)Sb\(_5\)Te\(_2\) and Fe\(_{0.125}\)Mo\(_3\)Sb\(_5\)Te\(_2\). These were chosen since direct calculations of 5% Fe would require a very large unit cell and too much time to calculate. Likewise, Mo\(_3\)Sb\(_{7-y}\)Te\(_y\) with y=1.5, 1.6, 1.7 would require too large a unit cell for a timely calculation of the DOS.

The DOS calculations (Fig. 1.6) show how interstitial doping of Fe into the semiconducting Mo\(_3\)Sb\(_5\)Te\(_2\) lowers the Fermi level and reduces the band gap. With 12.5% of Fe, the band gap is reduced to less than 0.1eV, which corresponds to a narrow gap semiconductor. The Fermi level, however, is lowered to the point where there are
about 20 states per eV, per cell. This corresponds to metallic behavior. It is conceivable that there may exist doping levels between 0% and 12.5% that will result in a degenerate semiconductor with few states at the Fermi level.

The previously investigated Mo$_3$Sb$_{5.4}$Te$_{1.6}$ has been measured to have a ZT of 0.8 at 1050K.[15] Adding 6% Ni interstitially into the matrix has resulted in an increase in ZT to 0.96 at 1000K.[16] Further investigations into the effect of the tellurium content on ZT, alongside experiments in the effectiveness of various metal ion dopants as a means to lower thermal conductivity were performed and the results are presented in this work.
Fig. 1.5a $\text{Ir}_2\text{Ge}_{12}$ Double Antiprism Chains

Source: Dr. Holger Kleinke, University of Waterloo, Waterloo, Canada
Fig. 1.5b Three Dimensional Ir₃Ge₇

Source: Dr. Holger Kleinke, University of Waterloo, Waterloo, Canada
Fig. 1.6  DOS Calculations of $\text{Mo}_3\text{Sb}_5\text{Te}_2$ and $\text{Fe}_{0.125}\text{Mo}_3\text{Sb}_5\text{Te}_2$
Processing and Measurement Systems

HIP (Hot Isostatic Press)

The hot isostatic press (HIP) is so called due to its ability to heat the sample while dynamically pressing it with a constant force. Both temperature and force are programmable. The system chamber consists of a fixed graphite ram above and a traveling graphite ram below. The rams are surrounded by a suspended cylindrical graphite heating element. Surrounding the element is graphite felt insulation, and finally the water-cooled metal chamber jacket (Fig. 1.7).

The pressing dies are made of semiconductor grade graphite housed inside a stainless steel jacket. The punches are made of molybdenum based TZM. Between the sample powders and each TZM rod circular disks of sheet graphite are placed to prevent surface reactions.

SPS (Spark Plasma Sintering)

In contrast to the HIP which uses heat and pressure to increase grain sizes, spark plasma sintering (SPS) uses high DC pulse current and the contact resistance between sample grains to weld the powders together without significant grain boundary growth. This results in higher density samples in significantly less time than those processed by a hot isostatic pressing.
The SPS system’s sample chamber (Fig. 1.8) consists of two large electrodes, a fixed one above and a lower one atop a pressing ram capable of forces up to 5-10 kN. In between, the die and punch assembly containing the sample powders sits between several large graphite spacers. These spacers assist in thermally distancing the electrodes from the die. Inserted into the side of the die is a thermocouple for temperature measurement during processing up to 1000°C. For temperatures from 1000°C up to 3000°C, a digital radiation thermometer (DRT) is used. The DRT is placed just outside the chamber and in front of a viewing glass. The thermocouple is removed from the die and placed aside so that the DRT’s line of sight is directed at the thermocouple hole in the die.

The SPS can operate under various atmospheres. Equipped with both a rotary and mechanical booster vacuum pump, the SPS can achieve a 6 Pa vacuum. The SPS is also set up with a gas inlet and outlet to allow for sintering under any inert gas or atmospheric air. While the SPS chamber can accommodate dies over 3” in diameter, only three die sizes are currently available for sample synthesis: 15 mm, 20 mm, and 0.5” inside diameter (sample size). Even though the system is capable of producing 50 kN of force, typical force applied to a 15mm die is 5-8 kN, resulting in 7-11 MPa. The maximum sintering temperature of the system is 2000°C.

**High Temperature Thermal Conductivity**

Acquiring thermal conductivity data above room temperature requires a two step process. First, a differential scanning calorimeter (DSC) is used to measure specific heat
capacity at a constant pressure, $c_p$. Second, a laser flash analysis system (LFA) is used to measure thermal diffusivity, $D$. Given the difference between $c_p$ and $c_v$ for a metal is within the error bars of the DSC measurement, thermal conductivity can be calculated using the density, $\rho$, and the following equation.

$$\kappa = \rho c_D = \rho c_p D$$ (1.31)

The DSC (Figs. 1.9a, 1.9b) utilizes the dependence on heat capacity of the rate of change of the temperature with respect to the heat inputted ($dT/dQ$), and the fact that heat capacity is sample dependent, to determine a relative heat capacity between a sample and a standard.

As the chamber heats up at a constant rate ($dQ/dt$), the sample carrier, crucibles, and anything they may contain absorb the heat energy and experience a change in temperature ($dT/dt$) that can be measured as a function of time. Dividing the heating rate by the derivative of the temperature with respect to time will yield heat capacity.

$$\frac{dQ}{dT} = mc_p = C_p$$ (1.32)

Using the set heating rate of the system and the directly measured temperature of the thermocouple will, however, yield the heat capacity of the sample, crucible, thermocouple, and sample carrier. Several measurements are required to account for these terms. First, $dQ/dT$ is compared between the two empty crucibles to obtain a baseline. The thermocouple voltage difference theoretically should be zero. However, since the two crucibles, both sides of the sample carrier, and the two thermocouples are
not identical, this step is necessary so that any apparent difference in $c_p$ due to the system may be negated. Second, a standard with a known $c_p$ is measured against the empty reference crucible. Finally the sample is measured. Once the baseline is subtracted from both the standard and sample data, a comparison may be made and the $c_p$ of the sample calculated.

The LFA system uses an unfocused laser to input heat into a sample from the bottom. An infrared detector is placed directly above the sample and records the temperature rise as a function of time (Fig. 1.10). Analysis of the temperature as a function of time data yields the thermal diffusivity through the following equation:

$$D = \frac{0.1388 l^2}{t_{1/2}}$$

(1.33)

where $l$ is the thickness of the sample and $t_{1/2}$ is the half-time of the temperature rise (Fig. 1.11). All samples with any amount of reflectivity are coated with graphite to maximize laser absorption.

**High Temperature Seebeck and Resistivity**

High temperature Seebeck and resistivity are measured simultaneously using a commercial system by ULVAC. The system can measure up to 800°C in a low pressure inert atmosphere using two probe heads, one being fixed and the other adjustable for clamping the sample. Thermocouples are attached to each probe head for an absolute
temperature reading. These two thermocouples are used to measure the temperature difference across the sample. One thermocouple is also placed outside a metallic shield that covers both probe heads. Additionally, two adjustable probes (towards or away from the sample) mounted perpendicular to the sample are set to make mechanical contact at a set distance apart from each other (Fig. 1.12).

Resistance measurements are made as current is passed through a standard resistor in series with the sample. The voltage drop across the standard is measured and used to accurately calculate the current into the sample through the upper and lower probe heads. The resistance of the sample between the lateral probes can be calculated by dividing the voltage difference between the probes by the current through the sample. Current is then reversed in order to subtract out thermal voltage from the Seebeck effect. Additionally, resistivity can be calculated using Eq. 1.8.

**Low Temperature Specific Heat Capacity and Hall Coefficient**

All low temperature specific heat capacity and hall coefficient measurements were taken on the commercial Physical Properties Measurement System (PPMS) by Quantum Design (QD). The PPMS is capable of measuring many low temperature transport properties from 2 K to 300 K.

Specific heat capacity is measured on a QD Heat Capacity Puck (Fig.13). The sample platform is suspended from the puck base by the wires attached to the heater and
thermocouple. First, an addendum data file is made by running the system with the puck and a small amount of thermal grease on its sample stage. The system is run a second time with the sample set in the thermal grease. In each run the heater inputs heat into the sample to establish a temperature difference from the base. After the heater is turned off, the sample cools as heat flows from the sample to the base via the connecting wires. This relaxation time is measured and compared to that of the addendum. All calculations are done by intrinsic software.
Fig. 1.7 Hot Isostatic Press Chamber
Fig. 1.8 Spark Plasma Sintering System
Fig. 1.9a Netzsch DSC 404 C Pegasus

Source: Netzsch “DSC 404 C Pegasus System Components”
Fig. 1.9b  Netzsch DSC 404C Pegasus Sample Carrier

Source: Netzsch “DSC 404C Pegasus System Components”
Fig. 1.10 Netzsch LFA 457 Microflash

Source: Netzsch “Operating Instructions: LFA 457 Microflash”
Fig. 1.11 LFA Temperature vs. Time

Source: A. Lindemann, J. Blumm “The NETZSCH LFA Series Instruments and Theory”
Fig. 1.12 High Temp R&S (ULVAC ZEM-2) Probe Head
Fig. 1.13  PPMS Heat Capacity Puck
PROCEDURE

Sample Synthesis

Powder Preparation

All the precursor powders were prepared at the University of Waterloo, Waterloo Canada by Dr. Holger Kleinke and his group. The subsequent pellets were densified using a hot isostatic press (HIP) at Clemson University.

Powder preparation began with mixing the elements (all purities >99.5%) in stoichiometric ratios according to the reaction equation:

\[
(0.05)X + 3Mo + (7 - y)Sb + (y)Te \rightarrow X_{0.05}Mo_3Sb_{7-y}Te_y
\]  

\[X=\{\text{Mn, Fe, Co, Ni}\} \text{ and } y=\{1.5, 1.6, 1.7\}\]

Powders were then placed in silica tubes, evacuated to 10^{-3} mBar, and sealed. Placed in a resistance furnace and heated to final cooking temperature of 500°C within 3 to 5 hours, the powders were allowed to cook overnight. The furnace was then ramped up to 700°C over 2 hours and the powders left for one week. 700°C was chosen because it is well above the melting points of Te (450°C) and Sb (630°C) but lower than that of Mo (2620°C). This ensured the mobility of Te and Sb. Next, the silica tubes were removed, shaken, and replaced into the furnace at 700°C for one more week. Allowing such long reaction times increased the possibility of obtaining a homogeneous sample.

At the end of the second week the furnace power was turned off and the sample allowed was to cool. Once cooled, the annealed sample was ground and powder x-ray
diffraction (XRD) data was measured. If the sample was found to have only the correct phase, the powders were packaged and shipped to the Complex and Advanced Materials Lab (CAML) at Clemson University. Otherwise, the powders were resealed in silica tubes, placed in the furnace, and ramped up to 700°C over 6 hours and the two week, two step annealing process was then repeated.

Sample Densification

All samples were densified at CAML using a hot isostatic press from Thermal Technology® (model HP20-4560-20). About 1.5 grams of powders were placed into a graphite die with half-inch diameter TZM punches. Fe$_{0.05}$Mo$_3$Sb$_{5.3}$Te$_{1.7}$, being the only exception, was pressed using a 3/8” die. A disk of sheet graphite was inserted between each punch and the sample powder to prevent reaction. The powder was then cold pressed with 3 to 4 tons of force and placed into the HIP. The system chamber was evacuated to less than 130 mTorr and purged with industry grade argon or nitrogen. This cycle was repeated three times and on the third purge left continuous at 30ml/min with the system vent valve open.

All samples in this series were hot-pressed under the same conditions: 720°C, 175 MPa, and 1 hour hold time. Using a programmable temperature and pressure controller, the samples were pressed with the program set points shown in Fig. 2.1.
The samples are left to cool inside the die, which remains inside the HIP chamber under zero pressure from the ram (the ram is slightly lowered and turned off after the program ends). Once removed from the die, the sample is sanded to remove all graphite and then cut using a low speed diamond wheel saw. Ready for sample characterization, the sample is placed in a desiccator until measured.

**Transport Properties Measurements**

**High Temperature Heat Capacity**

A Netzsch DSC 404C Pegasus was used to measure the $c_p$ of each sample above room temperature as well as for locating decomposition peaks. Sample sizes measured were between 25 and 120 mg. Each sample was measured from room temperature to at least 700°C.

**High Temperature Thermal Diffusivity**

Using the Netzsch LFA 457 Microflash, thermal diffusivity was measured from 50°C to 500°C (323K to 773K) by steps of 50K with the exception of Fe$_{0.05}$Mo$_5$Sb$_{5.4}$Te$_{1.6}$ (Fe-1.6), which was measured up to 400°C (673K). All samples were cut into 8mm by 8mm square piece except Fe-1.6, which was measured as a 10mm diameter circular disk. All thicknesses were between 1.25mm and 2.38mm except, of course, Fe-1.6: 1.72mm.

Each sample was prepared by first sanding the surface smooth and then coating it with a thin layer of graphite, sprayed on to maximize laser absorption. Once the samples
were loaded, the system was evacuated with a mechanical pump for 3 or more minutes and then purged with industry grade argon gas. This was repeated at least two times with the final purge set to 75ml/min and the system vent valve open for a continuous flow.

**High Temperature Thermal Conductivity**

Thermal conductivity is related to thermal diffusivity, density, and specific heat capacity by Eq. 1.30. For high temperatures, the heat capacity at a constant volume approaches a constant value—the Dulong-Petit limit, which is calculated by Eq. 1.22. In calculating the thermal conductivity above room temperature, the density, which has a very weak dependence on temperature in this regime, was assumed constant and the room temperature value used. Additionally, the Dulong-Petit limit of $c_v$ (Fig. 2.2) was used as a constant value for determining thermal conductivity from diffusivity.

**High Temperature Resistivity and Seebeck**

With an ULVAC model ZEM-2 system, Seebeck and resistivity were simultaneously measured from 50°C to 700°C (323K to 973K) with data points taken every 50 K. Sample dimensions were 1 to 2 mm by 1 to 2 mm square and 6 to 8 mm long. All measurements were performed under a low pressure, high purity helium atmosphere.
Low Temperature Heat Capacity

Low temperature heat capacities were measured on select samples from 2 K to 300 K using the Physical Properties Measurement System (PPMS) from Quantum Design. To minimize heat loss, measurements were taken under a high vacuum. Thermal grease was also applied to the sample stage and the sample itself to maximize heat flux to the sample. Additionally, sample pieces with a flat, smooth side were chosen for making good contact with the sample stage and thus ensuring maximum heat flow. Sample masses were between 10 and 25 mg.

Hall Coefficient

The PPMS, paired with a specialized Hall measurement puck, was also used to make Hall coefficient measurements. Two samples where simultaneously measured using the five-probe method (Fig. 2.3). This technique uses geometry and the fact that the electric potential difference between two points on the surface of the sample is linearly proportional to the distance between them to find the Hall voltage between two points along a line perpendicular to the current flow, or, effectively, parallel to the cross-section. Hall measurements were taken from room temperature to 5 K on samples 1 to 2 mm thick by 2 to 4 mm wide by 6 to 8 mm long.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Duration (min:sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>min. (46 to 53)†</td>
<td>initial</td>
</tr>
<tr>
<td>0→720</td>
<td>min.</td>
<td>10:00</td>
</tr>
<tr>
<td>720</td>
<td>min.→174</td>
<td>05:30</td>
</tr>
<tr>
<td>720</td>
<td>174</td>
<td>60:00</td>
</tr>
<tr>
<td>720→0</td>
<td>174</td>
<td>05:00</td>
</tr>
<tr>
<td>0</td>
<td>174→min.</td>
<td>00:10</td>
</tr>
</tbody>
</table>

† This is the minimum per limitations of the system.

Fig. 2.1 HIP Program Set Points
<table>
<thead>
<tr>
<th>Xₙ,ₙ</th>
<th>Fe,1.5</th>
<th>Fe,1.6</th>
<th>Fe,1.7</th>
<th>Mn,1.6</th>
<th>Co,1.6</th>
<th>Ni,1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>cᵥ (J/g·K)</td>
<td>0.2177</td>
<td>0.2175</td>
<td>0.2174</td>
<td>0.2175</td>
<td>0.2175</td>
<td>0.2175</td>
</tr>
<tr>
<td>ρ (g/cm³)</td>
<td>8.73</td>
<td>8.64</td>
<td>8.73</td>
<td>8.78</td>
<td>8.65</td>
<td>8.80</td>
</tr>
</tbody>
</table>

Fig. 2.2 Densities and Dulong-Petit Limits of Cᵥ for All Samples
Fig. 2.3 Five-Probe Hall Measurement
RESULTS

$X_{0.05}Mo_{3}Sb_{7-y}Te_{y}$; $X$=Fe Sub-series

Electrical Transport Properties

Low temperature resistivity and Seebeck coefficient data was measured for the Fe sub-series using a custom-designed cryocooler system from 8 K to 310 K.[18] Any offsets between the high and low temperature data were adjusted for in the high temperature resistivity and Seebeck coefficient data reported in this section.

Fig 3.1 shows the high temperature electrical resistivity data of $Fe_{0.05}Mo_{3}Sb_{7-y}Te_{y}$ for $y=1.5$ (Fe-1.5), 1.6 (Fe-1.6), 1.7 (Fe-1.7), which exhibits a trend of increased resistivity with increasing tellurium content. Tellurium, having one more electron than antimony, decreases the majority carrier concentration, which is shown to be holes by the positive thermopower (Fig 3.2).

The temperature dependence of all three materials is such that resistivity increases with temperature, which is characteristic of a degenerate semiconductor. Fe-1.5 has the highest electrical conductivity starting at $1944 \, \Omega^{-1} \text{cm}^{-1}$ at 325 K, followed by Fe-1.6 with $1658 \, \Omega^{-1} \text{cm}^{-1}$ and Fe-1.7 with $1425 \, \Omega^{-1} \text{cm}^{-1}$.

The slopes of the resistivity versus temperature data varies between samples. The residual resistivity was subtracted by calculating the normalized-reduced resistivity of each sample. This was done in order to determine the relative temperature dependences of the resistivities of the samples. This was achieved by subtracting the
value of the resistivity at 10 K—extrapolated from a linear region of the low temperature
data (75 K to 200 K)—from each data point and then normalizing by the same value.
The normalized-reduced resistivity values are shown in Fig. 3.3. These values are the
same between the three samples within estimated uncertainties, verifying that all three
samples have the same linear temperature dependence of the resistivity, which increases
with temperature, thus showing a metallic-like behavior. The magnitudes of the
resistivities, however, suggest that they behave as heavily doped semiconductors.

The Seebeck coefficient of Fe-1.5, Fe-1.6, and Fe-1.7 is 51 \( \mu \text{V/K} \), 62 \( \mu \text{V/K} \), and
67 \( \mu \text{V/K} \), respectively, at 323 K. All three samples show a trend of increasing
thermopower with temperature, with Fe-1.6 reaching 165 \( \mu \text{V/K} \) at 956 K and Fe-1.7
reaching 195 \( \mu \text{V/K} \) at 958 K. The data shows a trend of increasing thermopower with
tellurium content. As tellurium’s extra electrons serve to lower the majority carrier
concentration of holes, this is consistent with thermopower’s usual trend of decreasing
with carrier concentration.

While the trend of decreasing electrical conductivity with tellurium content works
to reduce the power factor, the effect of an increase in the tellurium content on the
thermopower works to increase the power factor. These two factors working against each
other result in a maximum power factor being exhibited by Fe-1.7 \( (\text{Fe}_{0.05}\text{Mo}_3\text{Sb}_{5.4}\text{Te}_{1.7}) \).
At 323 K, the power factors of Fe-1.5, Fe-1.6, and Fe-1.7 are 0.17 Wm\(^{-1}\)K\(^{-1}\), 0.20 Wm\(^{-1}\)K\(^{-1}\),
and 0.21 Wm\(^{-1}\)K\(^{-1}\), respectively. All three samples show a trend of increasing power
factor with respect to temperature (Fig. 3.4).
Fe-1.6 reached a maximum power factor value of 2.0 Wm\(^{-1}\)K\(^{-1}\) at 956 K. At 958 K, the power factor of Fe-1.7 reached a maximum of 2.1 Wm\(^{-1}\)K\(^{-1}\). The electrical properties of Fe-1.5 were only measured to 613 K due to equipment failure. The power factor at that temperature was 0.78 Wm\(^{-1}\)K\(^{-1}\). Having power factors on the order of 2 Wm\(^{-1}\)K\(^{-1}\) at temperatures near 1000 K demonstrates these materials to be competitive thermoelectric materials.

**Thermal Transport Properties**

Fig. 3.5 and Fig. 3.6 show the temperature dependence of the thermal diffusivity and thermal conductivity values of Fe\(_{0.05}\)Mo\(_3\)Sb\(_{7-y}\)Te\(_y\) for \(y=1.5\) (Fe-1.5), 1.6 (Fe-1.6), 1.7 (Fe-1.7). All thermal conductivity values were calculated using Eq. 1.31. The Dulong-Petit limit was used as a constant \(C_V\). This method is considered valid since all the calculations were done for temperatures above the Debye temperature of each sample. Low temperature \(C_P\) data and Debye temperature data for Fe-1.5 is presented in Fig. 3.7.

The change in the slope of the thermal diffusivity values can be attributed to its partial dependence on the resistivity of the system as modeled by the Wiedemann-Franz relation: \(\kappa_e = \sigma L_e T\). Fig. 3.8 shows the total, electronic, and lattice thermal conductivity values of Fe-1.6. The lattice contributions to the thermal conductivity values of all three samples, by subtraction of the electronic contributions, are shown in Fig. 3.9. Shown with a \(1/T\) fit lines for each data set, Fig. 3.9 suggests that the dominating scattering mechanism is high temperature U-process scattering of phonons.
Lattice thermal conductivity is expected to decrease with mass fluctuation—the alternation of Sb and Te atoms in the lattice. The more evenly split the ratio between Sb and Te is, the higher the mass fluctuation, and the lower the lattice thermal conductivity, presumably. However, the opposite is observed in the X=Fe sub-series. Fe-1.5 starts off at about 3.5 Wm$^{-1}$K$^{-1}$ at 323K. At the same temperature, Fe-1.6 was found to have a lattice thermal conductivity of 3.9 Wm$^{-1}$K$^{-1}$ and that of Fe-1.7 was measured to be 4.3 Wm$^{-1}$K$^{-1}$. At an average temperature of 617K, the lattice thermal conductivity values were measured to be 2.1 Wm$^{-1}$K$^{-1}$, 2.4 Wm$^{-1}$K$^{-1}$, 2.3 Wm$^{-1}$K$^{-1}$ for Fe-1.5, Fe.16, and Fe-1.7 respectively. Since a measured value of thermal conductivity, as well as electrical resistivity, depends on many extrinsic factors, such as dimension, grain size, and density, it is worth noting that the densities of all three samples (Fig. 2.2) were all measured to be within a 2% difference of each other.

The negative temperature dependence of the lattice—and therefore the total—thermal conductivity is a result of high temperature U-process interactions (Umklapp scattering) becoming more and more dominant as temperature increases. The total thermal conductivity is almost invariant for all samples throughout the entire high temperature regime and show a weaker temperature dependence than the lattice thermal conductivity. This is due to the electronic contribution to the thermal conductivity increasing with temperature and, therefore, counterbalancing the decreasing lattice thermal conductivity. Near-room temperature values are between 5 and 5.5 Wm$^{-1}$K$^{-1}$ and decrease with temperature to between 3.5 and 4 Wm$^{-1}$K$^{-1}$ at about 775 K.
Figure-of-Merit

Perhaps a more useful analysis of transport properties of related materials of a particular family can be made by considering the ratio of electrical and thermal conductivities (\(\sigma/\kappa\)). To maximize this value is to approach phonon glass-electron crystal type behavior, which is a concept of a material exhibiting very low, glass-like thermal conductivity while maintaining very high electrical conductivity as found in crystalline solids.

When measured on a bulk polycrystalline sample, the electrical conductivity is closely coupled to the thermal conductivity, as they both depend on extrinsic factors such as density, grain size, and sample dimensions. Comparing \(\sigma/\kappa\) between materials in a systematically varied series makes it possible to investigate their abilities to transport heat and charge while negating the effects of extrinsic factors. Fig. 3.10 presents the \(\sigma/\kappa\) of the samples in the X=Fe sub-series. This ratio, to which ZT is proportional, decreases with tellurium content, resulting in Fe-1.5 exhibiting the largest \(\sigma/\kappa\) value. The thermopower, as previously discussed, increases with tellurium content. In this balancing act, so to speak, results in Fe 1.6 and Fe-1.7 having nearly the same ZT (Fig. 3.11) throughout the temperature regime, both staying above Fe-1.5. At 323 K, Fe-1.6 and Fe-1.7 have a ZT of 0.039, as compared to 0.033 at the same temperature for Fe-1.5. At 660 K the ZT of Fe-1.6 and Fe-1.7 was calculated to be 0.25. Fe-1.5 was not measured up to that temperature.
These ZT values were calculated using interpolated thermal conductivity data. The thermal diffusivity was fitted with a third degree polynomial fit and then recalculated at the temperatures of the resistivity and thermopower measurements. The thermal conductivity was then recalculated using this interpolated diffusivity data. A table of room temperature and maximum values of all measured properties is presented in Figs. 3.12a and 3.12b.
Fig. 3.1 High Temperature Electrical Resistivity of X=Fe Samples
Fig. 3.2 High Temperature Thermopower of X=Fe Samples
Fig. 3.3 High Temperature Normalized-Reduced Resistivity of X=Fe Samples
Fig. 3.4 High Temperature Power Factor of X=Fe Samples
Fig. 3.5 High Temperature Thermal Diffusivity of X=Fe Samples
Fig. 3.6 High Temperature Thermal Conductivity of X=Fe Samples
Fig. 3.7 Low Temperature $C_p$ and Debye Temperature of Fe-1.5

$\gamma = 20.015 \text{ mJ} \cdot \text{mol}^{-1} \text{K}^{-2}$

$\beta = 0.386 \text{ mJ} \cdot \text{mol}^{-1} \text{K}^{-4}$

$\theta_D = 370 \text{ K}$
Fig. 3.8  High Temperature Total, Electrical (Wiedemann-Franz), and Lattice Thermal Conductivity of Fe-1.6
Fig. 3.9 High Temperature Lattice Thermal Conductivity of X=Fe Samples
Fig. 3.10 High Temperature Electrical to Thermal Conductivity Ratio of X=Fe Samples
Fig. 3.11 Dimensionless Figure-of-Merit of X=Fe Samples
### Room Temperature Values

<table>
<thead>
<tr>
<th></th>
<th>Temp. (K)</th>
<th>Seebeck (µV/K)*</th>
<th>Resistivity (mΩ·cm)*</th>
<th>P.F. (Wm⁻¹k⁻¹)</th>
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<th>Temp. (K)</th>
<th>Seebeck (µV/K)*</th>
<th>Resistivity (mΩ·cm)*</th>
<th>P.F. (Wm⁻¹k⁻¹)</th>
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<td>0.51</td>
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<td>195</td>
<td>1.73</td>
<td>2.1</td>
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*High temperature resistivity and Seebeck values are scaled to align with low temperature values.*

### Room Temperature Values

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<thead>
<tr>
<th></th>
<th>Temp. (K)</th>
<th>κ_TOTAL (Wm⁻¹k⁻¹)</th>
<th>κ_LATTICE (Wm⁻¹k⁻¹)</th>
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<th>Temp. (K)</th>
<th>κ_TOTAL (Wm⁻¹k⁻¹)</th>
<th>κ_LATTICE (Wm⁻¹k⁻¹)</th>
<th>Debye Temp.</th>
<th>Maximum ZT</th>
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<td>4.2</td>
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<td>0.19 @ 613K</td>
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<td></td>
<td>659</td>
<td>4.0</td>
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<td>4.3</td>
<td></td>
<td>758</td>
<td>3.6</td>
<td>2.3</td>
<td>---</td>
<td>0.34 @ 758K</td>
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Fig. 3.12a Room Temperature and Maximum Values of Electrical Properties of X=Fe Sub-series.

Fig. 3.12b Room Temperature and Maximum Values of Thermal Properties of X=Fe Sub-series.
$X_{0.05}\text{Mo}_3\text{Sb}_{7.7}\text{Te}_y; y=1.6 \text{ Sub-series}$

Electrical Transport Properties

Low temperature resistivity and Seebeck coefficient data of the samples in the $y=1.6$ sub-series was not measured, with the exception of Fe-1.6. Therefore, the raw data of Fe-1.6, unadjusted, is reported here for a fair comparison of the effects of the filler atom species on thermoelectric properties.

High temperature electrical resistivity data ($\rho$) of $X_{0.05}\text{Mo}_3\text{Sb}_{5.4}\text{Te}_{1.6}$ with $X=\text{Mn (Mn-1.6), Fe (Fe-1.6), Co (Co-1.6), Ni (Ni-1.6)}$ is presented in Fig 3.13. While all four materials show a somewhat linear temperature dependence that increases with temperature, there does not appear to be an obvious trend relating the resistivity to the filler atom species. In order of increasing atomic number, the filler atoms are Mn, Fe, Co and then Ni. Mn-1.6 exhibits the lowest resistivity near room temperature of 0.658 mΩ·cm at 324 K. Fe-1.6 was found to have a resistivity of 0.718 mΩ·cm at 324 K. The resistivity values of Co-1.6 and Ni-1.6 fell in between these two with $\rho$ equaling 0.657 mΩ·cm at 324 K for Ni-1.6 and 0.703 mΩ·cm at 322 K for Co-1.6. As with the $X=\text{Fe}$ samples, the linear resistivity that increases with temperature is consistent with metallic-like or degenerate semiconductor behavior. The magnitudes of the resistivity and thermopower, however, suggest a heavily doped semiconductor. At about 957 K, Fe-1.6 and Ni-1.6 resistivity values reach 1.40 mΩ·cm and 1.33 mΩ·cm, respectively.

As with the resistivity, the thermopower data (Fig. 3.14) of the $y=1.6$ sub-series samples exhibit now particular trend linking the Seebeck coefficient to filler atom
species. The temperature dependence of all four samples is very linear up to 670 K and increases with temperature. All values are positive, revealing the samples to be p-type. Co-1.6 exhibits the lowest thermopower of 51 µV/K at 324 K. At 324 K, the Seebeck coefficients of Mn-1.6, Fe-1.6, and Ni-1.6 were measured to be 55 µV/K, 60 µV/K, and 56 µV/K, respectively.

Filler atom species was shown to have little effect on the power factor (Fig. 3.15). At 324 K the power factor of Mn-1.6, Fe-1.6 and Ni-1.6 are 0.15 Wm⁻¹K⁻¹, 0.16 Wm⁻¹K⁻¹, 0.15 Wm⁻¹K⁻¹, respectively. The power factor of Co-1.6 at 322 K was calculated to be 0.12 Wm⁻¹K⁻¹. With the exception of Co-1.6, which was measured only to 560 K at which p.f.=0.48 Wm⁻¹K⁻¹, the power factors of Mn-1.6, Fe-1.6, and Ni-1.6 were within error bars of each other. Measured to 762 K, the power factor of Mn-1.6 reached 1.12 Wm⁻¹K⁻¹. Near 957 K, Fe.16 and Ni-1.6 exhibit a very similar power factor of 1.8 Wm⁻¹K⁻¹ and 1.9 Wm⁻¹K⁻¹, respectively. This compares nicely to data published on Mo₃Sb₁.₄Te₁.₆ by F. Gascoin et al.[15], which presented resistivity and thermopower data that suggested a power factor of about 1.8 Wm⁻¹K⁻¹ at 960 K.

Thermal Transport Properties

Filler atoms were introduced in hopes of lower thermal conductivity through “rattling,” and thus scattering phonons. The size and atomic number of the atoms plays a large role in their effectiveness as a scattering mechanism. Thermal conductivity as a function of atomic number is not expected to follow a direct correlation. For atoms with
small atomic radii, phonons will be easily absorb and their momentum transmitted to the atoms resulting in motion of the atoms being in phase with the phonons, and therefore the phonons will not be scattered. If their radii are too large, the atoms will fill the cage and densify the sample, thus increasing thermal conductivity. When the atoms have mass and radii that fall in between, there is a possibility that the phonons will induce anharmonic motion with respect to the phonons, thus scattering them.

Thermal diffusivity and thermal conductivity data of the sub-series $X_{0.05}Mo_{3}Sb_{5.4}Te_{1.6}$ for $X=$Mn (Mn-1.5), Fe (Fe-1.6), Co (Co-1.6), Ni (Ni-1.6) is presented in Fig. 3.16 and Fig. 3.17, respectively. Thermal conductivity values were calculated using Eq. 1.31 with the Dulong-Petit limit used as $C_V$. Specific heat capacity and Debye temperature data are presented for Mn-1.6 (Fig. 3.18) and Ni-1.6 (Fig. 3.19).

All samples exhibit a temperature dependence such that thermal conductivity decreases with temperature with a $T^{-1}$ dependence. As in the $X=$Fe sub-series, this is due to the increasing dominance of U-process scattering at high temperatures. The total thermal conductivity values of Mn-1.6, Fe-1.6, Co-1.6, and Ni-1.6 at 322 K are 5.4 Wm$^{-1}$K$^{-1}$, 5.2 Wm$^{-1}$K$^{-1}$, 5.7 Wm$^{-1}$K$^{-1}$, and 5.6 Wm$^{-1}$K$^{-1}$, respectively. Fe-1.6 continues to have the lowest thermal conductivity, with a lowest measured value of 4.0 Wm$^{-1}$K$^{-1}$ at 673 K. Near the same temperature, Mn-1.6, Co-1.6, and Ni-1.6 have thermal conductivity values of 4.2 Wm$^{-1}$K$^{-1}$, 4.1 Wm$^{-1}$K$^{-1}$, and 4.3 Wm$^{-1}$K$^{-1}$, respectively. These thermal conductivity values are significantly higher than those reported for the undoped $Mo_{3}Sb_{5.4}Te_{1.6}$ by F. Gascoin et al.—4.0 Wm$^{-1}$K$^{-1}$ at 370 K and 3.1 Wm$^{-1}$K$^{-1}$ at 670 K.
Lattice thermal conductivity values (Fig. 3.20) were calculated by subtracting the electronic contribution as calculated by the Wiedemann-Franz relation.

**Figure-of-Merit**

The material in this sub-series with the highest calculated ZT (Fig. 3.21) is again Fe-1.6. As reported in the previous section, Fe-1.6 exhibits a ZT of 0.03 at 323 K, and 0.22 at 660 K. The next most efficient material was Mn-1.6, with a ZT of 0.03 at 323 K, and rising up to 0.28 at 762 K. While the ZT of Ni-1.6 was below these two throughout most of the temperature regime (300 K-800 K), it was measured to be near the same value at the highest temperature measured—0.29 at 766 K. Because of the curvature of the ZT vs T graphs, it is easy to infer that the ZT of Ni-1.6 may surpass that of Mn-1.6 in the temperature range of 800 K to 1000 K. Co-1.6 exhibited the lowest ZT with values of 0.02 at 322 K and 0.10 at 560 K. A table of room temperature and maximum values of all measured properties is presented in Figs. 3.22a and 3.22b.
Fig. 3.13 High Temperature Electrical Resistivity of y=1.6 Samples
Fig. 3.14 High Temperature Thermopower of y=1.6 Samples
Fig. 3.15 High Temperature Power Factor of $y=1.6$ Samples

[Graph showing the power factor versus temperature for different samples with varying composition.]
Fig. 3.16  High Temperature Thermal Diffusivity of $y=1.6$ Samples
Fig. 3.17  High Temperature Thermal Conductivity of y=1.6 Samples
\[
\gamma = 15.779 \text{ mJ\cdot mol}^{-1}\text{K}^{-2}
\]
\[
\beta = 0.647 \text{ mJ\cdot mol}^{-1}\text{K}^{-4}
\]
\[
\theta_D = 311 \text{ K}
\]

Fig. 3.18  Low Temperature $C_p$ and Debye Temperature of Mn-1.6
\[
\begin{align*}
\gamma &= 15.277 \text{ mJ} \cdot \text{mol}^{-1} \text{K}^{-2} \\
\beta &= 0.430 \text{ mJ} \cdot \text{mol}^{-1} \text{K}^{-4} \\
\theta_D &= 357 \text{ K}
\end{align*}
\]

Fig. 3.19  Low Temperature $C_P$ and Debye Temperature of Ni-1.6
Fig. 3.20 High Temperature Lattice Thermal Conductivity of $y=1.6$ Samples
Fig. 3.21 Dimensionless Figure-of-Merit of y=1.6 Samples
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<td>Co-1.6</td>
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<td>Ni-1.6</td>
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Fig. 3.22a Room Temperature and Maximum Values of Electrical Properties of y=1.6 Sub-series.

*High temperature resistivity and Seebeck values are not scaled to align with low temperature values.

<table>
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<tr>
<th>Room Temperature Values</th>
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<td>κLATTICE (Wm⁻¹K⁻¹)</td>
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<tr>
<td>Ni-1.6</td>
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Fig. 3.22b Room Temperature and Maximum Values of Thermal Properties of y=1.6 Sub-series.
CONCLUSION

The thermoelectric properties of $X_{0.05}Mo_3Sb_{7-y}Te_y$ were studied from two approaches—by varying the Sb-Te ratio while using one specie of filler atom (X=Fe), and then independently varying the filler transition metal atomic number while keeping the Sb-Te ratio fixed (y=1.6). From the first approach, the results show that both the Seebeck coefficient and electrical resistivity increased with tellurium content, as expected. There is no clear trend, however, in the thermal conductivity as the values are all very similar, and most likely within error bars of each other. Fe-1.6 (X=Fe, y=1.6) and Fe-1.7 (X=Fe, y=1.6) showed the highest ZT of 0.21 at 610 K while Fe-1.5 exhibited the lowest ZT value of 0.19 at 613 K. It is notable, however, that the ZT values of all three samples in the sub-series are very similar.

The second approach, attempting to maximize ZT through lower thermal conductivity via interstitially doped “rattler” atoms, proved a failure. For all samples in the y=1.6 sub-series (X=Mn, Fe, Co, Ni) the thermal conductivity values were higher and than that of the $Mo_3Sb_{5.4}Te_{1.6}$ parent compound, which has been reported by Hong Xu et al. to start at about 4.5 Wm$^{-1}$K$^{-1}$ at room temperature and decrease with temperature to about 3.5 Wm$^{-1}$K$^{-1}$ at 750 K (all samples in y=1.6 sub-series have values above 5 Wm$^{-1}$K$^{-1}$ at 325 K and remain above 4.0 Wm$^{-1}$K$^{-1}$ at 600 K).[16] The electrical properties were, however, comparable to the parent compound, with power factors ranging from 0.12 Wm$^{-1}$K$^{-1}$ (X=Co) to 0.17 Wm$^{-1}$K$^{-1}$ (X=Fe) at 322 K, as compared to a power factor of 0.16 Wm$^{-1}$K$^{-1}$ at 323 K for $Mo_3Sb_{5.4}Te_{1.6}$.[16]
Future work may include investigating various doping levels of the transition metal ions (between 5% and 12.5%) as well as investigating the use of other dopant species.
REFERENCES


