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Rare Earth Chalcogenides for Use as High Temperature
Thermoelectric Materials

by

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ABSTRACT

In the first part of my thesis, the electrical resistivity, thermoelectric power (Seebeck coefficient) and Hall effect have been measured in $X_y(Y_2S_3)_{1-y}$ (where $y = Cu, B$ or Al) compounds with the δ -monoclinic structure at the composition of $y = 0.05$ for Cu and B , and in the composition range of $0.025 \leq y \leq 0.075$ for Al , in order to determine their potential as high temperature ($300 - 1000^\circ C$) thermoelectric materials. The Cu and B doped (via mechanical alloying) Y_2S_3 are insulators and not good thermoelectrics. The Al -doped Y_2S_3 behaves as a metastable degenerate semiconductor with itinerant conduction. The room temperature electrical resistivity decreases as the aluminum doping level increases, where the room temperature Seebeck coefficient remains constant at around $400 \mu V/^\circ C$ regardless of the aluminum doping level. These materials, however, become insulators after two weeks heat treatment at $1000^\circ C$ or higher, indicating their metastable state. Both the electrical resistivity and Seebeck coefficient increased with increasing temperature, and showed lower values of both while being cooled to room temperature, further indicating a metastable state. The behavior of the Seebeck coefficient was not adequately explained, but it is suggested that this metastable state is caused by the aluminum atoms being forced into the interstitial sites of the Y_2S_3 lattice, where it acts as a current carrier donor. When heated, it is suggested that these atoms diffuse to electrically insulated positions, increasing resistivity, and making an insulator. The largest power factor value did not exceed $0.6 \mu W/cm-^\circ C^2$, and decreased with increasing temperature. The results of this study indicate that Cu, B , and Al doped Y_2S_3 are not useful as high temperature thermoelectric materials.

In the second part of my thesis, the phase stability of the γ -cubic $LaSe_{1.47(1.48)}$ and $NdSe_{1.47}$ compounds with the Th_3P_3 type structure, along with their electrical resistivity, Seebeck coefficient, and Hall effect (when possible) were measured periodically as the materials were annealed at $800^\circ C$ or $1000^\circ C$ to determine their potential as thermoelectric materials for long term applications at high temperatures. These materials in the $300-1000$

$^{\circ}\text{C}$ range behave as degenerate semiconductors with itinerant conduction. The $\text{LaSe}_{1.47(1.48)}$ samples showed the presence of a second phase, which is a ternary oxide with a tetragonal structure called the β -phase. The content of this phase increased with increasing anneal time, where the $\text{NdSe}_{1.47}$ samples show no sign of this second phase. The room temperature electrical resistivities, Seebeck coefficients and power factors of the $\text{LaSe}_{1.47(1.48)}$ samples tended to decrease with increased annealing time, which was attributed to the increasing presence of the β -phase. The electrical resistivities and Seebeck coefficients of the $\text{NdSe}_{1.47}$ samples tended to decrease, while the power factor remained relatively stable between 0.7 and $1.5\mu\text{W}/\text{cm}\cdot^{\circ}\text{C}^2$ with increased annealing times. The high temperature electrical resistivity and Seebeck coefficient for $\text{LaSe}_{1.47}$ and $\text{NdSe}_{1.47}$ increased with increasing temperature throughout the temperature range of room temperature to 1000°C . The power factor however peaks of $5.2\mu\text{W}/\text{cm}\cdot^{\circ}\text{C}^2$ at 800°C for $\text{LaSe}_{1.47}$ and $1.45\mu\text{W}/\text{cm}\cdot^{\circ}\text{C}^2$ at 500°C for $\text{NdSe}_{1.47}$. This leads to the conclusion that $\text{LaSe}_{1.47(1.48)}$ is not promising for use as a high temperature thermoelectric material due to the phase transformation from γ to β , where the $\text{NdSe}_{1.47}$ shows no such transformation, and is an encouraging prospect for this application.

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GENERAL INTRODUCTION

The two major self contained power sources used in recent history have been chemical batteries and solar power. This presents a problem for such applications in which these are wholly inadequate. This includes applications where sunlight is not available at sufficient intensity, and the duration of operation is several years long. The answer for such applications in the past has been the radioisotope thermoelectric generator (RTG). Such generators have been used in the NASA Pioneer, Voyager, Viking, Galileo, and Ulysses space missions with a great deal of success.¹ These devices work by using the Seebeck effect to convert the heat energy from a decaying radioisotope directly into electrical energy.² The primary radioisotopes that has been used as heat sources for the RTG's is plutonium-238.¹

Theoretical Background

The Seebeck effect occurs when a thermal gradient is imposed upon a material, which is originally at a uniform temperature and carrier concentration. When one end of the sample is heated, the current carriers at the warmer end of the material are put into a higher energy state. Thus the carriers diffuse towards the cooler end of the material, and a lower energy state. The resulting gradient in carrier concentration creates a charge imbalance and a voltage potential in the opposite direction of the thermally induced current. This potential can be harnessed to generate a current in a circuit, and used to operate devices.^{2,3}

For thermoelectric power generators, the efficiency of energy conversion is the most important factor when considering the generator's output and cost. The maximum conversion efficiency ($\eta_{\max}$) for the thermocouple shown in Figure 1 is:

$$\eta_{\max} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + Z\bar{T}} + 1}{\sqrt{1 + Z\bar{T}} + (T_c + T_h)} \quad (1)$$

Figure 1. Thermoelectric couple as used in power generators

where T_h = temperature of the hot junction, T_c = temperature of the cold junction, $\bar{T} = (T_h + T_c) / 2$ and Z = the combined figure of merit of the thermocouple, and is equal to:

$$Z = \frac{(S_n - S_p)^2}{[(\rho_n \kappa_n)^{1/2} + (\rho_p \kappa_p)^{1/2}]^2} \quad (2)$$

where S_n = Seebeck coefficient of the n-type semiconductor, S_p = Seebeck coefficient of the p-type semiconductor, ρ_n = electrical resistivity of the n-type semiconductor, ρ_p = electrical resistance of the p-type semiconductor, κ_n = thermal conductivity of the n-type semiconductor, and κ_p = thermal conductivity of p-type semiconductor.⁴

The first part of equation (1) is the thermodynamic efficiency of an irreversible Carnot engine. The second part is the reduction in efficiency due to irreversible energy loss through heat conduction along the thermocouples, and, Joulean heat losses.⁴ It is apparent from this equation that in order to maximize efficiency, one must maximize the factor $Z\bar{T}$. In other words one must obtain as high a value of the figure of merit over as wide a temperature range as possible. The figure of merit for a single material is given by:⁵

$$Z = \frac{S^2}{\rho \kappa} \quad (3)$$

The Seebeck coefficient (S) is the voltage potential that is generated for each degree of temperature difference between the hot and cold junctions of the thermocouple. If the Seebeck coefficient is negative, the materials is a n-type semiconductor, and if it is positive, the material is a p-type semiconductor. It decreases with increasing carrier concentration, and as such tends to zero for metals.³ The resistivity ($\rho=1/\sigma$ where σ = electrical conductivity) is the ratio between the voltage applied to a material and the current density that the voltage generates. This is dependent upon the carrier

concentration and mobility of the material. The thermal conductivity (κ) is the thermal current divided by the temperature gradient that is causing this current. For a unipolar conductor, this effect can be attributed to two mechanisms, which are:⁶

$$\kappa = \kappa_{el} + \kappa_{ph} \quad (4)$$

Where κ_{el} is the electrical component, and κ_{ph} is the phonon component in this equation. The first contribution is due to thermal energy being absorbed by electrons, and then moving to a different position and transferring its energy to that position. The second component is due to the thermal energy being transferred via lattice vibrations, or phonons.

Considering these factors, when one endeavors to choose an appropriate material for a thermoelectric application, electrical insulators and metals can be ruled out. Insulators have very high Seebeck coefficients, but their resistivity is too high to allow current flow from the power generator. Metals have low resistivities and thus large current flow, but their Seebeck coefficients are of negligible size. It turns out that the power factor (S^2/ρ or $S^2\sigma$) is maximized for heavily doped or near degenerate semiconductors with carrier concentrations within the approximate range of 10^{19} to 10^{20} . This is graphically shown in the schematic plot of Seebeck coefficient, resistivity, power factor, and thermal conductivity versus carrier concentration in Figure 2.² These factors are complex functions of the Fermi energy and the carrier concentration which are dependent upon the energy band structure of the material being considered.³

This leads to the three desired characteristics of a good thermoelectric material:³

- High Seebeck coefficient, to maximize voltage potential.
- Low resistivity, to minimize Joulian energy losses.

Figure 2: Plots which show the dependence of Seebeck coefficient (S), electrical conductivity (σ), thermal conductivity (κ), and power factor ($S^2\sigma$) on the carrier concentration (n).

- Small thermal conductivity, to better retain thermal gradient across the thermoelement by minimizing the heat lost through thermal conduction from the hot to the cold ends.

Rare Earth Chalcogenides

Over the past 3 decades there have been many materials that have been studied as thermoelectric materials, including silicon germanium alloys,^{7,8} bismuth tellurides,^{5,9} lead tellurides,^{5,10} rare earth chalcogenides,^{11,12} boron rich borides,¹³ and chemical vapor deposited (CVD) carbon fibers.¹⁴ From these possibilities, one that has been given a lot of attention for high temperature applications are the rare earth chalcogenides with the Th_3P_4 defect structure. This high-temperature γ -phase forms a cubic defect structure over the composition range R_3X_4 to R_2X_3 (where R = rare earth metal and X = S, Se, or Te).¹⁵ These materials have received this attention because of their high melting points,¹⁵ low thermal conductivities,^{12,16} and ability to self dope from an insulator to a metallic conductor by changing the composition of the material.^{16,17} The formula unit cell can be written as $4(\text{R}_{3-y}\text{v}_y\text{X}_4)$, where v represents a rare earth metal vacancy and $0 \leq y \leq 1/3$.^{11,15} This ability to self dope occurs as the material goes from a metallic conductor to an insulator as the rare earth metal content decreases through the γ -phase composition range, or as y in the equation above varies from zero to one third.

The mechanism for this self doping ability is apparent when one considers the charge balance over the γ -phase composition range. For the composition where $y = 1/3$ in the formula given above (i.e., R_2X_3), there is an average of 1/4 vacancy, two R^{3+} ions that contribute 6 electrons, and three X^{2-} ions, accepting 6 electrons per unit cell. Since there is no charge imbalance, there are no current carriers, so it is an insulator. For the composition where $y = 0$ (i.e., R_3X_4), there are no vacancies, three R^{3+} ions contributing 9 electrons, and four X^{2-} ions accepting eight electrons per unit cell. This leaves 1 electron per formula unit free to conduct electricity, making it a metallic conductor.

Eventhough the thermoelectric properties of rare earth sulfides have been widely investigated, to this point, almost exclusively the rare earth sulfides with the high temperature γ -phase (Th_3P_4 defect structure) have been considered.^{12,18-21} The study covered in the first part of this thesis focused on doped yttrium sesquisulfide with the η -orthorhombic structure. This compound system is of interest as a high temperature thermoelectric material because of its high melting point,²² and due to its chemical and crystallographic similarities with dysprosium sesquisulfide²³, its expected low thermal conductivity,²⁴ and large band gap.²⁵ The similarity between yttrium and dysprosium sesquisulfide also makes the yttrium sulfide look promising because of the promising thermoelectric properties shown by dysprosium sesquisulfide when doped with copper.²⁴

The second part of this thesis will be concerned with the thermoelectric properties, and phase composition of lanthanum and neodymium selenides ($\text{LaSe}_{1.47}$, $\text{LaSe}_{1.48}$ and $\text{NdSe}_{1.47}$). I plan to show whether, and at what rate these materials transform from the γ -phase, with the Th_3P_4 cubic defect structure, to the ternary oxide β -phase, with a tetragonal crystal structure,²⁶⁻³⁰ during long term annealing at high temperatures. I will also show the effect that this heat treatment has on the thermoelectric properties of the selenides.

Mechanical Alloying and Mechanical Milling

Mechanical alloying was used in the processing of all of the yttrium sesquisulfide samples and some of the lanthanum and neodymium selenide samples. Mechanical alloying is a dry, non-equilibrium, high energy ball milling process that was first developed in the early 1960's to make oxide dispersion strengthened superalloys.^{31,32} This technique allows the combination of two materials with widely differing melting points, and has been used to produce nanocrystalline structures,³³ intermetallic compounds,³⁴ solid solutions,²⁴ and amorphization^{35,36} that would be difficult or impossible to achieve any

other way. It is believed to work by a balance between fracturing and cold welding of the materials during repeated impacts, that alloys them at an atomic level.³² Mechanical Milling is a process similar to mechanical alloying except only one component is subjected to the ball milling, which creates metastable crystal structures. Examples of this are the bcc structures that form in AlZr,³⁷ the fcc structure found in 50:50 Zr-Cr,³⁸ and the amorphous structures in Nb₃Sn³⁹ Ni₃Al.⁴⁰ This process also changes many rare earth sesquisulfides (R₂S₃), from its room temperature and pressure structures to the high pressure γ -cubic, with the Th₃P₄ defect type structure,⁴¹ which is metastable at ambient conditions (i.e. room temperature and 1 atmosphere of pressure). The transformation of yttrium sesquisulfide (Y₂S₃) from its room temperature and pressure δ - monoclinic structure to the high pressure γ -structure was observed by Han et al.^{23,41} However, there is no such phase transformation shown in the lanthanum and neodymium selenides. This has a direct bearing on this thesis for obvious reasons.

PART 1: THERMOELECTRIC PROPERTIES OF YTTRIUM SESQUISULFIDE
(Y_2S_3) MECHANICALLY ALLOYED WITH COPPER, BORON,
AND ALUMINUM

INTRODUCTION

Yttrium sulfide was chosen for study as a high temperature thermoelectric material in part because of its high melting point,²² and its expected low thermal conductivity^{23,24} and large band gap.^{23,25} However, the main reason for this interest is the chemical and crystallographic similarities yttrium sesquisulfide has with dysprosium sesquisulfide,²³ which Han et al showed to have encouraging thermoelectric properties when doped with copper via mechanical alloying.²⁴ It is hoped that yttrium sulfide doped via mechanical alloying will show good thermoelectric properties.

Dopants

The dopants chosen for this study are copper, boron and aluminum. Copper was chosen as one of the dopants because of the promising results that Han *et al* obtained from dysprosium sesquisulfide (Dy_2S_3) that was mechanically alloyed with copper.²⁴ He found that this created an n-type semiconductor (electrons as current carriers) with carrier concentrations within the desired (10^{19} to 10^{20} cm^{-3}) range. Boron was chosen because it is a commonly used dopant in applications such as in p-type silicon germanium thermoelectric materials.⁷ It is suspected that the boron atom is small enough to fit into the interstitial spaces of the yttrium sulfide lattice, where its +3 valence should donate excess electrons, creating an n-type conductor. Adding excess aluminum was attempted to see what effect a dopant of similar size and valence to yttrium would have on the thermoelectric properties of the sulfide.

EXPERIMENTAL PROCEDURES

Production of Yttrium Sesquisulfide (Y_2S_3)

High purity yttrium (prepared by the Materials Preparation Center, Ames Laboratory) was electropolished to remove oxides and other impurities from the surface of the metal. The yttrium sesquisulfide was prepared by sealing stoichiometric amounts of yttrium and sulphur (99.999 at% pure, purchased from the American Smelting and Refining Co.) in a quartz ampoule with iodine (~10mg), under a helium atmosphere. After being sealed, the ampoule contents were heated to 500°C and held for one day. It was then heated to 650°C to vaporize the sulphur. After the sulfur was vaporized, the temperature of the sample was increased by 100°C per day. This was continued until 950°C was reached, where it was left at for 3 days in order to homogenize the sample. It was then air cooled to ambient room temperature.

Alloying the Sulfide

The desired amounts of copper (99.99 at% pure, purchased from the AESAR Co.), boron (99.7% pure, purchases from the Johnson Matthey Catalog Co.), or aluminum, were placed in a tungsten carbide (WC) lined vial with the yttrium sulfide, and three 10mm diameter tungsten carbide balls. The sample to ball weight ratio was in the range of 1:5 to 1:6. The vial was hermetically sealed in a helium filled glove box, using O-rings and electrical tape placed on the seams, that maintained the internal inert helium atmosphere. The contents of the vial were then mechanically alloyed for 6 hours with a Spex 8000 mixer/mill.

Hot Pressing

The mechanically alloyed powder was loaded into a half inch graphite die inside a helium filled glove box. The loaded die was then transported to a hot pressing apparatus in a helium filled plastic bag, and mounted between a piston and base. The vacuum

chamber of the press was evacuated to approximately 10^{-7} torr. The powders were heated to 1100°C , and placed under a pressure of 138MPa (20ksi), and held there for one hour. It was then slowly cooled to ambient temperature, as shown in Figure 3.

X-Ray Analysis

The crystal structures of the as mechanically alloyed and as hot pressed $\text{D}_x(\text{Y}_2\text{S}_3)_{1-x}$ (where D = Cu, B, or Al and $x = 0.025$ to 0.075) were characterized with a SINTAG PAD-V X-ray diffractometer using copper K-alpha radiation.

Heat Treatment

Some of the aluminum-doped, hot pressed samples were heat treated at either 1000°C or 1100°C for two weeks. The samples were protected from the atmosphere by double sealing them in a tantalum crucible and then a quartz ampoule, under an inert helium atmosphere. Heating and cooling rates were minimized to $2^{\circ}\text{C}/\text{min}$ to avoid crack formation in samples due to thermal shock.

Hall Effect Measurements

The electrical resistivity of the doped yttrium sulfide compounds were measured at room temperature using the van der Pauw technique.^{42,43} Several measurements were taken at currents below 5mA (depending on how much current could be gotten through the sample) and then averaged. The carrier concentration was measured at the same current as the van der Pauw resistivity, under a magnetic field of 1 tesla. Hall mobilities (μ) were calculated using the relationships between Hall coefficient (R_H), carrier concentration (n), and electrical resistivity ($R_H = 1/ne$ and $\rho = 1/n\mu$, where e = electronic charge).

High Temperature Electrical Resistivity and Seebeck Coefficient

The electrical resistivity was measured using a standard dc four-point probe technique.⁴⁴ The Seebeck coefficient was measured using the slope of the thermal emf

Figure 3: Temperature and pressure schedule for hot pressing yttrium sesquisulfide.

versus temperature plot method.⁴⁵ Both measurements were made simultaneously on the same sample in a vacuum chamber at approximately 10^{-6} torr. These measurements were taken over the temperature range of room temperature to 1000°C , using a computer controlled heating and data acquisition system.

Metallography

Photomicrographs were taken of the as-hot pressed and as-heat treated samples. These samples were etched with a solution of 2% nitric acid and 98% methanol.

RESULTS AND DISCUSSION

The yttrium sesquisulfide used in these thesis experiments shows a structural change while undergoing mechanical alloying. This material is stable as a monoclinic, δ -phase structure at room temperature and pressure,²³ as shown in the x-ray diffraction pattern in Figure 4(a). At atmospheric pressure, this material maintains this structure from room temperature to its melting point. However, as the pressure on the sulfide is increased, its phase changes from its δ -monoclinic structure to its γ -phase structure with the cubic Th_3P_4 defect structure. The yttrium sulfide samples dealt with in this study showed this transformation to the high pressure phase after 6 hours of mechanical alloying, as was found by Han et al.³⁴ They also showed that when the sample materials are hot pressed at 1100°C, this transformation was reversed, and the metastable γ -phase gives way to the atmospheric pressure δ -phase. The x-ray diffraction patterns of the γ -phase and the as hot pressed δ -phase, of a sample mechanically alloyed with 5at% copper can be seen in Figures 4(b) and 4(c) respectively. This transformation was the same for all samples studied, regardless of the dopant or its concentration.

Thermoelectric Properties

A summary of the room temperature power factor data, dopant, and dopant level of the mechanically alloyed yttrium sulfide samples is shown in Table 1. The sample that was mechanically milled with no dopant turned out to be an insulator. This is no surprise considering the charge balance argument given in the rare earth chalcogenide section of the Introduction. The next sections will explore what difference the presence of the dopants have on the properties of this electrically insulating material.

Yttrium Sesquisulfide Doped with 5at% Copper

According to the sign of the room temperature Hall coefficient (i.e. positive), this sample is a p-type conductor. Three measurements of the resistivity were taken, which

Figure 4: X-ray patterns for Y_2S_3 : (a) before being mechanically alloyed; (b) after being mechanically alloyed with 5at% Cu; (c) after being hot pressed at 1100°C and 138MPa for one hour.

Table 1: Dopants and Power Factor Data for Mechanically Alloyed Y_2S_3

Dopant and Dopant Level	Current Hall Measurement was taken at (mA)	Van der Pauw Resistivity (mOhm-cm)	Carrier Conc. (cm^{-3})	Hall Mobilities ($cm^2/V-s$)	Seebeck Coefficients ($\mu V/^\circ C$)
no dopant	***	***	***	***	***
5at% Cu	1.0×10^{-2}	7.76×10^{19}	1.14×10^9	< 0.001	***
5at% B	***	***	***	***	***
2.5at% Al	NA	NA	NA	NA	-413
5at% Al	1.0	2018	5.38×10^{17}	5.75	-397
	NA	NA	NA	NA	-404
5at% Al, After 2 weeks @ 1100°C	***	***	***	***	***
5at% Al, After 2 weeks @ 1000°C	***	***	***	***	***
7.5at% Al	5.0	1678	1.45×10^{18}	2.57	-411

*** - Resistivity was too high for measurements to be taken

NA - Measurements are not available due to equipment failure

ranged in value from 5.817×10^{19} to 1.163×10^{20} m Ω -cm. This plainly indicates that this alloy is a very good insulating material, which is a disappointment when considering the promising results gotten from dysprosium sesquisulfide when mechanically alloyed with copper.²⁴ One possible mechanism by which the high resistivity, p-type conduction occurs is that the copper atoms replace the yttrium atoms within the sulfide lattice. The +1 valence of the copper atom, when replacing the +3 valence of the yttrium atom would leave two electron-hole current carriers per inclusion of a copper atom. This model could account for the p-type conducting character found in this sample, but it has a problem in that with a doping level of 5at%, one would expect a larger carrier concentration.

Yttrium Sesquisulfide Doped with 5at% Boron

The Y₂S₃ sample that was mechanically alloyed with boron is a very good insulator. As indicated in Table 1, its resistivity was too high to be able to measure it with existing equipment. Obviously, the boron did not behave as desired, and did not reside in the interstitial spaces of the sulfide lattice and act as a carrier donor. Considering the differences in sizes between the yttrium and boron atoms, it is not likely that the boron atoms would occupy the yttrium lattice sites. More probably the boron did not alloy with the sulfide, leaving free boron ions in within the sample in small enough concentrations so as not to show up on x-ray diffraction patterns.

Yttrium Sesquisulfide Doped with Various Amounts of Aluminum

The resistivity of the sulfide doped with 5at% aluminum was such an improvement over the materials doped with copper and boron that further investigation was undertaken. Two more samples of the sulfide were made by mechanically alloying them with 2.5at% and 7.5at% aluminum and then analyzed.

Hall Measurements of Al Doped Samples

Table 1 shows that the Hall effect data for the material doped with 2.5at% aluminum is not available. This is because its resistivity is too high to be measured with the available Hall effect apparatus, using the available software. The software that is required for the Hall effect measurement of high resistivity samples using the computer controlled data acquisition system now in place, is not available. However, such software was used earlier on a different computer acquisition system to measure the Hall properties of the material doped with copper, but is no longer available. With the existing data, the only assumption that can be made concerning the electrical properties of the material alloyed with 2.5% aluminum is that it has a higher resistivity than the materials doped with 5% and 7.5% aluminum.

Using this assumption, the data indicates that the resistivity of the material decreases with increasing aluminum dopant level. Since a material's electrical resistivity is a measure of that material's resistance to the movement of electrons within the sample under an electric field, it depends both on the carrier concentration and Hall mobility. From the measured carrier concentrations of the materials alloyed with 5at% and 7.5at% aluminum, apparently the presence of aluminum increases the carrier concentration, and decreases the resistivity. However, the presence of aluminum in the materials seems to have the opposite effect on the Hall mobility. This is consistent with what Zhuze et al¹⁶ reported for R_2X_3 compounds (where $R = La, Pr, Ce$ or Nd , and $X = S, Se$, or Te) at constant temperature. He reported that the Hall mobility decreases with increasing carrier concentration.

It is also worth noticing that the photomicrographs of the samples mechanically alloyed with 2.5at%, 5at% and 7.5at% aluminum (shown in Figures 5, 6 and 7) show evidence of a second phase, the content of which increases with increasing aluminum

Figure 5: Photomicrograph of a Y_2S_3 sample mechanically alloyed with 2.5at% aluminum (magnification = 1000X).

Figure 6: Photomicrograph of a Y_2S_3 sample mechanically alloyed with 5at% aluminum (magnification = 1000X).

Figure 7: Photomicrograph of a Y_2S_3 sample mechanically alloyed with 7.5at% aluminum (magnification = 1000X).

concentration. This phase does not appear to be pure crystalline aluminum or aluminum sulfide, because the x-ray diffraction pattern of the sample that was doped with 7.5at% aluminum does not show the presence of a second phase. However, since the appearance of this second phase increases with increasing aluminum content, it can be assumed that it is an aluminum rich phase, which is confirmed by EDS. Assuming that this second phase has a significantly lower resistivity than the rest of the sulfide matrix, the increased presence of this phase could account for at least part of the decrease in resistivity with increasing aluminum content.

Another feature found in the Hall effect measurements of the heat treated samples alloyed with 5at% aluminum is that they became insulators after soaking the samples for two weeks at temperatures at or greater than 1000°C. As with the undoped and boron-doped yttrium sesquisulfide samples, the resistivity was so high that not enough current could be generated from a thermal gradient to get a dependable Seebeck coefficient measurement. This indicates that the as hot-pressed samples are in a metastable state, which is responsible for their improved electrical properties. This is supported by the photomicrograph of this sample shown in Figure 8. It shows almost none of the light colored second phase shown in the photomicrograph before heat treatment (Figure 6), but it seems to show a different phase, which appears black and was not present before heat treatment.

One possible model for this occurrence is that the mechanical alloying process forced the aluminum atoms into the interstitial sites of the host crystal lattice. This could explain why no crystal structure other than the δ -phase Y_2S_3 is indicated by x-ray diffraction analysis, yet the samples are still semiconductors. Since the aluminum is extraneous to the sulfide lattice, it would have no corresponding ions to act as electron acceptors. Thus the +3 valence of the aluminum would donate three current carrying

Figure 8: Micrograph of a Y_2S_3 sample mechanically alloyed with 5at% aluminum, after a 2 weeks anneal at 1000°C (magnification = 1000X).

electrons per interstitial inclusion. When the material is annealed at high temperatures, over time the heat would allow the aluminum atoms to diffuse out of the interstitial sites, where they could collect at the surface of the sample or the phase boundaries, and no longer be able to donate current carriers to the δ -phase material. The atoms also would not have enough connectivity between them to provide a current path through the entire sample along the phase boundaries, therefore their valence electrons would no longer be current carriers. This aluminum could also oxidize, for, despite being double sealed in a helium atmosphere, there is always a small amount of oxygen present in the helium gas, and additional oxygen can be present due to the storage of tantalum crucible and sulfide samples in air. The oxidized aluminum could be indicated by the black areas shown at the phase boundaries in the photomicrograph of the heat treated sample (Figure 8).

Another possibility is that, since the aluminum atoms have a similar size and valence to the yttrium atoms, it is possible that they take the place of the yttrium atoms in the lattice, where their valence electrons would be compensated for by sulfur ions. The excess yttrium atoms could then diffuse to the sample's surface and possibly oxidize, tying down their valence electrons in with the oxygen acceptors. The isolated positions of the yttrium atoms would also prohibit enough contact between them to create a current path through the sample. Thus making their valence electrons unable to be current carriers, even if the yttrium did not oxidize.

Although speculative, these models would account for the inverse relationship between the current carrier concentration and the Hall mobility, because, as more aluminum atoms are forced into the metastable interstitial positions, the carrier concentrations would increase. This would also significantly effect the Hall mobility, for as the atoms are squeezed into the interstitial sites, the resulting distortion in the crystalline matrix and lattice potentials from having such a large atom in the interstitial

positions would obstruct current paths, and in general slow the current carriers, i.e. decrease the Hall mobility of the material. When one looks at the ability of mechanical alloying to create metastable crystal and amorphous atomic structures, this is a likely explanation.

Room Temperature Seebeck Coefficient of Al Doped Samples

The sign of the Seebeck coefficients shown in Table 1 indicate that all of the Al-doped Y_2S_3 samples are n-type conductors. Three consecutive measurements of the Seebeck coefficient were taken of one of the samples mechanically alloyed with 5at% aluminum. These values ranged from -397 to -416 $\mu V/^\circ C$, which is a discrepancy of 19 $\mu V/^\circ C$. The values of the Seebeck coefficients of the samples in Table 1 fall within 15 $\mu V/^\circ C$ of each other, indicating that the variation in Seebeck coefficient can be attributed to experimental error. Despite carrier concentrations, which vary as much as one order of magnitude, there is no significant difference in the values of the Seebeck coefficients for the aluminum doped samples. This is very unusual for rare earth sesquisulfides, for Cu-doped Dy_2S_3 ⁴⁶ and all RS_x and RSe_x (where $R = La$ to Nd , and $x = 1.33$ to 1.50) compounds⁴⁷ conform to a nearly free electron model.⁴⁸ This model, states that the values of the Seebeck coefficients (S) are given by:

$$S = \left(\frac{8\pi^2 k^2 T m^*}{3eh^2} \right) \left(\frac{\pi}{3n} \right)^{\frac{2}{3}} (1 + R) \quad (5)$$

where k = Boltzmann's constant, m^* = effective mass, h = Planck's constant, e = electronic charge, n = carrier concentration, T = absolute temperature, $R = (d \ln \lambda_s / d \ln E)_{E_F}$, λ_s is the scattering distance, E = kinetic energy, and E_F = Fermi energy. This model indicates that room temperature values of S vary as $n^{-2/3}$. I do not know why the aluminum-doped yttrium sesquisulfide does not conform. Perhaps after more carrier concentration data is available, it will become more apparent.

High Temperature Resistivity of Al Doped Samples

The plot of the high temperature data for the Y_2S_3 mechanically alloyed with 7.5at% Al, during heating and cooling, is shown in Figure 9. The lines in this figure are the regression plots of the best fit functions of the data points. The heating curve indicates that the sample is a metallic conductor, because the resistivity increases with increasing temperature.

The electrical resistivity consists of one temperature independent and two temperature dependent factors. These are as follows:⁴⁴

$$\rho_T = \rho_o + \rho_{iT} + \rho_{mT} \quad (6)$$

where ρ_T = total resistivity, ρ_o = residual resistivity due to impurities, defects and strains, ρ_{iT} = resistivity due to interaction between the current carriers and the lattice vibrations, and ρ_{mT} = resistivity due to magnetic disorder, which becomes a constant above the magnetic ordering temperature. For this material, the ρ_{mT} term is zero because there are no magnetic ions in Al-doped Y_2S_3 . As a result, the temperature dependence of the electrical resistivity can be narrowed down to the interactions between the current carriers and the crystalline lattice. The increase in resistivity with increasing temperature could also be caused, at least in part, by aluminum atoms diffusing from the interstitial sites to the yttrium lattice sites. This possibility is supported by the fact that the cooling curve decreases to the resistivity levels much higher than observed in the heating curve. This certainly indicates some change occurring in the metastable condition. This would however only effect the resistivity at higher temperatures, thereby explaining the higher rate of increase in resistivity in the approximate temperature range of 500°C to 700°C.

The electrical resistivity reaches a maximum at around 800°C, for either heating or cooling. one explanation for this is intrinsic conduction.⁴⁹ This results from thermal

Figure 9: Resistivity versus temperature for a Y_2S_3 sample mechanically alloyed with 7.5at% Al.

excitation of electrons, leaving the same number of holes in the valence band. It creates a conductor with equal electron and hole current carriers. This effect harms the thermoelectric properties of a material, and needs to be avoided. It causes a significant decrease in the Seebeck coefficient (because of the higher carrier concentration), and increases the thermal conductivity from an ambipolar contribution due to the diffusion of excitons from the high temperature end to the low temperature end. In the case of yttrium sulfide however, the expected large band gap^{23,25} would shift the onset of this thermal generation of electron-hole (excitons) to higher temperatures, for more thermal energy is needed to allow the electrons to bridge the band gap. This is why large energy band gaps are desirable characteristics for high temperature thermoelectric materials. However, because of these materials' characteristics, it is unlikely that intrinsic conduction is the cause for the decrease in electrical resistivity above 800°C. This is supported by the fact that many other rare earth chalcogenides, including LaS_x (where $x = 1.33$ to 1.50), Nd_3S_4 , Nd_3Te_4 , and La_3Te_4 , the carrier concentrations are virtually invariant with temperature, but are dependent on composition alone, i.e. the chalcogen to rare earth ratio.

When considering electrical resistivity in Al-doped Y_2S_3 , the carrier concentration depends only on the electrical activity of the Al in the Y_2S_3 matrix, since it is solely responsible for the conducting behavior. It would be expected that as the Al dopant becomes more electrically active with increasing temperature, the carrier concentration would also increase. Hence, the electrical resistivity should begin to decrease at high temperatures.

High Temperature Seebeck Coefficient of Al Doped Samples

The high temperature Seebeck coefficient data for the Y_2S_3 sample that was mechanically alloyed with 7.5at% Al is shown in Figure 10. The values of the Seebeck

Figure 10: Seebeck Coefficient versus Temperature for a Y_2S_3 Sample Doped with 7.5at% Al.

coefficient increase linearly with temperature, further indicating that the material is an n-type semiconductor with metallic type conduction. The linearity of the curve between room temperature and 700°C is consistent with the model of aluminum atoms diffusing to where they are electrically isolated, reducing the carrier concentration at higher temperatures. This linear increase ends at approximately 700°C. As indicated for the high temperature electrical resistivity data, this behavior of the Seebeck coefficient is not due to intrinsic conduction. It is possibly due to the enhancement in the carrier concentration due to the high temperature. This however is not consistent with the room temperature Seebeck coefficient values, which seemed to be approximately the same regardless of the carrier concentration.

The most puzzling thing about this data is the Seebeck coefficient values shown in the cooling curve. If the carrier concentration in the material is lower while the data for the cooling curve was being taken, as is suggested by the high temperature resistivity data, one would expect the Seebeck coefficient to increase.⁴⁸ This is however not the case. The Seebeck coefficient decreases while measurements were being taken during cooling. It seems to indicate that the carrier concentration is larger during the cooling of the sample, which is contrary with the idea that aluminum atoms are diffusing from the metastable interstitial sites of the Y_2S_3 crystalline structure to electrically inert positions, yet it does suggest the change of a metastable state. One possible explanation is that microcracks formed in the sample while heating, which gave an inflated value for electrical resistivity, while the carrier concentration was actually increasing. This however does not seem likely, when it is known that long term heat treatment causes the carrier concentration to decrease to near zero. I can not say why else the material would behave this way.

High Temperature Power Factor of Al Doped Samples

The power factor (S^2/ρ) is an extremely important materials property when considering the overall effectiveness of a thermoelectric material. High temperature power factors for a Y_2S_3 sample mechanically alloyed with 7.5at% Al were calculated from the resistivity and Seebeck coefficient data, and the results displayed in Figure 11. This plainly shows that the power factor decreases with increasing temperature and then levels off in the range of 700°C to 1000°C, with a minimum value of $0.121 \mu W/cm-^{\circ}C^2$. The data for the cooling curve stays relatively constant through the temperature range of 1000°C to 370°C during cooling. This is rather disappointing, because Han et al⁴⁶ found that copper-doped dysprosium sesquisulfide had power factor values that increased with increasing temperature, and had maximum values of $7.7 \mu W/cm-^{\circ}C^2$. The reason for the differences was already discussed with the component properties.

Most of the evidence supports the model that says that aluminum atoms are forced into the metastable position of the interstitial sites in the yttrium sulfide lattice by the mechanical alloying process, and then diffusing to electrically insulated positions outside the sulfide lattice, and then perhaps oxidizing when heated. This accounts for why the material is not an insulator like the boron and copper doped yttrium sulfide, yet becomes one when heat treated. The only evidence to refute this is the high temperature Seebeck coefficient data. Why this behaves inconsistently with the rest of the data, I do not know. Hopefully it will become clearer as more carrier concentration and metallography data becomes available.

This decrease in power factor over such a short time of being held at high temperatures, not to mention the materials conversion to an insulator after annealing at 1000°C or more for two weeks, does not make this material a very promising candidate for use as a high temperature thermoelectric. The room temperature power factor of less

Figure 11: Power Factor versus Temperature for a Y_2S_3 sample mechanically alloyed with 7.5at% Al.

than $1\mu\text{W}/\text{cm}\cdot^{\circ}\text{C}^2$ is also not sufficient for this application. This and the fact that, part of the thermoelectric properties present might be attributable to the presence of a different crystallographic phase leads me to come to the conclusion that, in the search for a high temperature thermoelectric material, yttrium sesquisulfide doped via mechanical alloying can be ruled out.

PART II: THERMOELECTRIC PROPERTIES OF LONG TERM HEAT TREATED
LANTHANUM AND NEODYMIUM SESQUISELENIDE, OF THE
STOICHIOMETRY $\text{RSe}_{1.47}$, AND $\text{RSe}_{1.48}$

INTRODUCTION

One group of materials within the rare earth chalcogenides with the Th_3P_4 crystal structure that have been studied as possible high temperature thermoelectric materials are the light lanthanide sulfides and selenides with stoichiometries between $\text{RS}_{1.45}$ and $\text{RS}_{1.50}$ (where $\text{R} = \text{La, Ce, Pr, Nd}$).^{11,12} These compounds have been shown to have promising thermoelectric properties, but there is a problem with the use of these materials for high temperature applications. When they are exposed to high temperatures for extended periods of time, in most cases they change phase from the γ -cubic Th_3P_4 type structure to a ternary oxide phase ($\text{R}_{10}\text{X}_{14}\text{O}$, where $\text{R} = \text{La, Pr, Ce, or Nd}$, and $\text{X} = \text{S or Se}$) with a tetragonal structure known as the β -phase.²⁶⁻³⁰ The computer generated x-ray diffraction patterns of γ and β lanthanum selenides are seen in Figure 1 and Figure 2 respectively.^{30,50} The β -phase has inferior thermoelectric properties, and over time makes these materials useless for thermoelectric application.¹¹ This phase transformation has already been shown to occur in all of the compounds in question except neodymium sesquiselenide ($\text{Nd}_2\text{Se}_{3-x}$).²⁹ The presence or absence and rate of this transformation in the compounds $\text{NdSe}_{1.47}$, $\text{LaSe}_{1.47}$, and $\text{LaSe}_{1.48}$, and the effect long term annealing has on their thermoelectric properties is the focus of this Part II of this thesis.

Figure 1: The computer generated x-ray diffraction pattern of the γ -phase La_2Se_3 , with the cubic Th_3P_4 defect structure.

Figure 2: The computer generates x-ray diffraction pattern of the β -phase $\text{La}_{10}\text{Se}_{14}\text{O}$.

EXPERIMENTAL PROCEDURES

Production of Selenides (LaSe_x or NdSe_x , where $x = 1.47$ to 1.5)

The appropriate amounts of high purity lanthanum or neodymium (produced by the Materials Preparation Center, Ames Lab.) and selenium (99.999 at% pure, from the American Smelting and Refining Co.) that give the stoichiometries $\text{LaSe}_{1.47}$, $\text{LaSe}_{1.48}$, and $\text{NdSe}_{1.47}$, were sealed in a quartz ampoule. The mixture was then heated to 500°C for one day, and then heated to 650°C , where it was held until the selenium was completely vaporized. The temperature was then increased 100°C every day until 950°C was reached, and it was left at this temperature for three days. It was then air cooled to ambient temperature. The resulting material consisted of unreacted metal and substoichiometric rare earth sesquiselenide (R_2Se_3 , where $\text{R} = \text{La}$ or Nd) compound.

Homogenization (mechanical alloying and melting)

In order to get the proper composition, the pure metal had to be incorporated into the selenide homogeneously. The metal and selenide mixtures that were mechanically alloyed were loaded into tungsten carbide lined vials with three 10mm tungsten carbide balls, and sealed in a helium filled glove box. It was then mechanically alloyed for 4 hours and 15 minutes in a Spex 8000 mixer/mill, with a sample to ball weight ratio of approximately 1:4.5.

The melting technique involved sealing the metal/selenide mixture in a sealed tungsten crucible under a vacuum of about 10^{-7} torr, and then loading it into a vacuum induction furnace. The sample chamber of the furnace was evacuated to 10^{-6} torr, and the sample was heated to above 1900°C for 20 minutes. The furnace was then air cooled to ambient temperature. The resulting selenide material was then removed from the tungsten vial, and ground into a powder.

Hot Pressing

The mechanically alloyed, or the melted and ground powders, were loaded into a half inch graphite die inside a helium filled glove box. The loaded die was then transported to a hot pressing apparatus in a helium filled plastic bag. The vacuum chamber of the press was evacuated to approximately 10^{-7} torr. The powders were heated to 1125°C for neodymium selenide or 1175°C for lanthanum selenide, and placed under a pressure of 59MPa (86ksi), and held there for one hour. The sample was then slowly cooled to ambient temperature, as shown in figure 3.

Heat Treatment

The selenide samples were double sealed in a tantalum crucible inside a quartz ampoule, under an inert helium atmosphere. The samples were annealed for as long as five months at 1000°C, or for three months at 800°C, while being cooled periodically for characterization. Heating and cooling rates were minimized to 2°C/min to avoid crack formation in samples due to thermal shock. These periodic analyses consisted of four room temperature measurements:

Hall Effect Measurements

Resistivities, measured by the Van der Pauw technique.^{42,43} Measurements were taken at 45, 50, and 55 mA, and averaged. When possible, carrier concentrations were measured at 99 mA, under a magnetic field of 1 tesla. Hall mobilities were calculated from the relationships between the Hall coefficients, carrier concentrations, and resistivities that were discussed in Part 1 of this thesis.

Room Temperature Seebeck Coefficient

Room temperature Seebeck coefficient was measured using the slope of the thermal emf versus temperature plot method⁴⁵ in open air.

Figure 3: Temperature and pressure schedule for the hot pressing of LaSe_{1.47} and LaSe_{1.48}.

X-ray Diffraction Analysis

X-ray diffraction analysis was used to determine the approximate β -phase content of each sample, using the SINTAG PAD-V X-ray diffractometer using Cu K-alpha radiation. This was done by comparing the relative intensities of the x-ray patterns with their theoretical absolute intensities generated by CSD software⁵⁰ according to the relation:

$$\frac{C_{\beta}}{C_{\gamma}} = \frac{I_{\beta}}{I_{\gamma}} \frac{I_{\gamma}^{cal}}{I_{\beta}^{cal}}$$

where C_{β} = concentration of β -phase, C_{γ} = concentration of γ -phase, I_{β} = intensity of β -phase diffraction peak, I_{γ} = intensity of γ -phase peak, I_{β}^{cal} = theoretical absolute intensity of β -phase peak, and I_{γ}^{cal} = theoretical absolute intensity of γ -phase peak.

High Temperature Electrical Resistivity and Seebeck Coefficient

The measurement method used was discussed in Part 1 of this thesis.

Metallography

The method used was discussed in Part 1 of this thesis.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The lanthanum selenide materials ($\text{LaSe}_{1.47}$ and $\text{LaSe}_{1.48}$) were annealed for as long as 6 months, and x-ray diffraction analysis shows evidence of the presence of the $\text{La}_{10}\text{Se}_{14}\text{O}$, β -phase in all of the annealed and some of the as hot pressed samples. The β -phase Bragg reflection peaks from the 253 and 127 planes, along with one peak that was a combination of the 046 and 352 plane reflections, were found among the x-ray patterns of the samples, which consist primarily of the γ -phase, with the Th_3P_4 cubic defect structure, as seen in Figure 4. The relative intensities of the β and γ reflection peaks were used to determine the approximate β -phase content in the samples. The plot of the resulting values can be seen in Figure 5.

As was expected, the β -phase content increased with annealing time, except in the situation of the material that was annealed for only two weeks at 1000°C before it was first removed from the furnace and analyzed. After this two week period, x-ray diffraction analysis indicated approximately 13.5% β -phase content, while after another two and a half months at 1000°C , x-ray analysis indicated a β -phase content of approximately 1.4%. One possible explanation for this anomalous data is that, with the β -phase being an oxide, its formation would depend on the presence of oxygen in the immediate vicinity of the sample. Despite the precautions to prevent this (double sealing the sample in a helium atmosphere) there would always be very small amounts of oxygen in the tantalum crucible anyway, unless the tantalum crucible were gettered at 1800 to 2000°C and then never exposed to the air, and the helium was gettered by passing it over Zr metal at $\sim 800^\circ\text{C}$. The helium tank that is used to fill the crucibles can have as much as 10 ppm oxygen. What ever oxygen was present would start to react with the sample from its exterior, and in time diffuse its way into the sample's interior. Since the sample

Figure 4: A Portion of an x-ray diffraction pattern showing the intensities of the hkl peaks of the β -phase $\text{La}_{10}\text{Se}_{14}\text{O}$ that are used to determine phase content.

Figure 5: β -phase content versus annealing time for materials a) $\text{LaSe}_{1.47}$, mechanically alloyed, and annealed at 1000°C; b) $\text{LaSe}_{1.47}$, melted and annealed at 1000°C; c) the same treatment as b; d) $\text{LaSe}_{1.48}$, mechanically alloyed and annealed at 1000°C; e) $\text{LaSe}_{1.48}$, mechanically alloyed and annealed at 800°C.

in question had only two weeks for the oxygen to react with of the sample, the oxide may have only reacted on the exposed surfaces. This results in a thin layer of β -phase on the surface of the sample, making the x-ray diffraction data not representative of the entire sample being analyzed. If this is the case, it could have been prevented by my cutting a more representative portion out of the sample, and grinding it into a powder for x-ray diffraction analysis. Unfortunately, this was not possible, because I needed the sample in one piece for other measurements. This does however confirm the onset of the transformation from γ to β phases, and the development of significant amounts of β -phase within two weeks of annealing at 1000°C.

Beaudry et al²⁸ found that $\text{LaS}_{1.48}$ developed 10% β -phase after 60 days of annealing at 900°C. The exact stoichiometries of the materials in this study are not known, so the compositions presented are that of the materials as they were nominally mixed. But the data indicates that the transformation of the lanthanum selenides is much slower than those reported for the sulfides with similar compositions. In fact most samples started the annealing process with more β -phase than they gain during 3 months annealing at 1000°C or 800°C. It appears that the preparation procedure (hot pressing at 1175°C for an hour, and for some, melting at 1900°C for 20 minutes) affects the γ to β transformation more than a 3 month anneal at 1000°C. The higher temperatures used in hot pressing and melting would seem to have been held for too short a time to cause the transformation. Oxygen effects could account for a larger part of the accelerated transformation. If the presence of oxygen has a an effect on the γ to β transformation, as was found by Beaudry et al²⁸ and Besancon et al,²⁹ then it seems that higher oxygen contamination during this is part of the production could be the reason for the presence of β -phase before annealing begins. The hot pressing chamber, with all the thermal insulators made form carbon cloth that are stored in air, would have a higher internal oxygen

pressure than a tantalum crucible that was pumped to a pressure of 5 microns mercury and back filled with helium at least three times.

Another argument for the effect that oxygen has on the phase transition in question is the relatively wide variation in the β -phase content between samples. There was great attention to eliminating oxygen from melting, hot pressing and annealing vessels, yet the β -phase appears in widely differing amounts. This indicates that the smallest variation in oxygen exposure can have a significant effect on the phase formation, because there is only a very small difference in the oxygen content inside the tantalum annealing crucibles. With such a sensitivity to oxygen exposure, the surroundings which would allow the lanthanum selenide to be used as a high temperature thermoelectric material seem unattainable.

The x-ray diffraction analysis of the neodymium selenide ($\text{NdSe}_{1.47}$) materials showed no evidence of the presence of β -phase after annealing at 1000°C for as long as 5 months.

Room Temperature Hall Effect Measurements

The Van der Pauw resistivity and (when possible) Hall effect measurements were taken of all the as hot pressed samples, and also periodically during the annealing of all selenide materials ($\text{LaSe}_{1.47}$, $\text{LaSe}_{1.48}$, and $\text{NdSe}_{1.47}$). According to the sign of the Hall coefficients (negative), all materials are n-type conductors. In addition, all of the six individual Van der Pauw resistivity measurements taken for each sample varied no more than 2% from their average values.

The resistivity is dependent on the carrier concentration and Hall mobility. Plots of the carrier concentration and hall mobility versus resistivity can be seen in Figures 6 and 7, respectively. These plots show that the resistivity decreases with increasing carrier concentration, but not much correlation between the Hall mobility and resistivity is seen.

Figure 6: Carrier concentration versus resistivity for all selenide samples (neodymium and lanthanum selenides that were mechanically alloyed and hot pressed, and melted and hot pressed).

Figure 7: Hall mobility versus resistivity for all selenide samples (Nd and La selenides, mechanical alloyed and hot pressed, and melted and hot pressed).

However, when the mechanically alloyed and melting preparation methods, and the neodymium and lanthanum compositions are considered separately, resistivity does seem to decrease with increasing mobility within the sample's categories. However, Figure 8 does not seem to show a similar trend between the Hall mobility and carrier concentration. This data is more consistent with what Wood et al¹² reported, in that no trend of increasing Hall mobility with decreasing carrier concentration is found.

The lanthanum selenides (nominal $\text{LaSe}_{1.47}$ and $\text{LaSe}_{1.48}$) showed increasing resistivity with increasing β -phase content, and increasing annealing time (Figures 9 and 10 respectively), as expected. There is one apparent exception to this, as shown in both figures: the $\text{LaSe}_{1.48}$ composition, which was annealed at 800°C . This could be due to a metastable condition brought about by the mechanical alloying process, which disappears after annealing, making the measurements taken before annealing anomalous. This is not very likely, because no such anomalous readings were found in the other samples that were prepared by mechanical alloying. More probably this was caused by inhomogeneities within the sample, causing anomalous readings from the measurement of different portions of the sample. It was necessary to take measurements from different portions of some of the samples, because of fracturing in the samples during heat treatment.

The neodymium selenide seems to show decreasing electrical resistivities with increasing annealing times, as depicted in Figure 11. This may be caused by a greater number of electrically active electrons being introduced due to heat treatment. This however, should not be considering likely, for Zhuze¹⁵ found that Nd_3S_4 had a carrier concentration independent of temperature in the range of 300°C to 1100°C . Assuming a similarity between the sulfide and selenide, since there are no foreign dopants, it is unlikely that a materials carrier concentration would increase at high temperatures unless

Figure 8: Hall mobility versus carrier concentration for all selenide samples (as listed in the legend of the graph).

Figure 9: β -phase content versus resistivity for all lanthanum samples (labeled as seen on the plot legend).

Figure 10: Annealing time versus resistivity for all the lanthanum selenide samples (labeled as seen in plot legend).

Figure 11: Annealing time versus resistivity for the neodymium selenide samples (labeled as seen in the plot legend).

composition changes. There is another possible reason for this trend in the resistivity. During heat treatments that extend over several months, it is possible for small amounts of selenium to volatilize out of the sample due to the high vapor pressure of selenium. This would adjust the stoichiometry of the neodymium selenide away from the Nd_2Se_3 composition towards the Nd_3Se_4 stoichiometry, decreasing the resistivity via the self doping mechanism⁴⁷ discussed in the introduction of part one of this thesis. However, this trend was not observed in the La-Se alloys, but this could have been masked by the formation of the β -phase, see Figures 5 and 9.

It is also of interest to note that in Figures 7 through 11, all of the samples that were prepared by melting and then hot pressing have resistivities that are significantly lower than those for the samples that were mechanically alloyed and then hot pressed. This could be attributed to the method by which the samples were prepared. Being sealed in a vacuum at 1900°C is bound to cause changes, i.e. it is possible that small amounts of selenium evaporated from the compound while at 1900°C , under a 10^{-7} torr vacuum, even though the time was relatively short compared to the annealing times.

Room Temperature Seebeck Coefficient

Room temperature Seebeck coefficients were measured periodically during annealing of the samples. From the sign of these measurements, all selenides in this study are n-type conductors. From seven individual measurements of Seebeck coefficient on a single $\text{LaSe}_{1.47}$ sample and also a single $\text{NdSe}_{1.47}$ sample, no value varied more than 3% from the average of the measurements. Presumably, this would indicate a similar variation within all of the samples, but more experimentation would be necessary to determine this.

According to the nearly free electron model, the Seebeck coefficient (S) of a material varies as the materials carrier concentration to the negative two thirds power ($n^{-2/3}$).⁴⁸

Figure 12: Carrier concentration to the negative two thirds power versus Seebeck coefficient for the lanthanum and neodymium selenides.

Figure 12 shows a plot of S versus $n^{-2/3}$ for the neodymium and lanthanum selenide samples. This plot shows a good correlation between my data and this model. Figures 13 and 14 show the plots of how the Seebeck coefficient varies with annealing time for the lanthanum and neodymium selenides, respectively. The error bars on these plots represent the variation seen in the samples that were measured several times. The Seebeck coefficient seems to be following the same basic patterns as the room temperature resistivity. With the direct relation of both properties on the carrier concentration, it appears that the same factors effecting carrier concentration are affecting both the resistivity and Seebeck coefficients, especially since these trends are not apparently attributable to the trends in the Hall mobility.

Room Temperature Power Factor

The room temperature power factors (S^2/ρ) for the lanthanum and neodymium selenide samples were calculated from the Seebeck coefficients and resistivities. Plots of power factor versus annealing time for lanthanum and neodymium selenide can be seen in Figures 15 and 16, respectively. These plots show the power factor to be somewhat erratic. This is not surprising when one considers the 3% suspected variation in the Seebeck coefficient is squared in the power factor. Despite this, it appears that the power factors of the lanthanum selenides decreased with increased annealing time, and thereby, also with increasing β -phase content. Once again, this is as expected. The power factor values for the neodymium selenide materials seem relatively consistent over time. They all fall within the range of $0.7\mu\text{W}/\text{cm}\cdot^\circ\text{C}^2$ and $1.5\mu\text{W}/\text{cm}\cdot^\circ\text{C}^2$, and many seemed to increase with annealing time. After the first month of annealing, there is not a sample that has a power factor below $1\mu\text{W}/\text{cm}\cdot^\circ\text{C}^2$. The apparent resilience of the neodymium selenide against degradation from long term exposure to high temperatures is consistent with the absence of the β -phase formation in the NdSe_x samples and this makes NdSe_x a

Figure 13: Annealing time versus Seebeck coefficient for the lanthanum selenide samples ($\text{LaSe}_{1.47}$ and $\text{LaSe}_{1.48}$). The error bar on the sample annealed for 5 months represents the variation in Seebeck coefficient found in seven individual measurements on the same sample.

Figure 14: Annealing time versus Seebeck coefficient for the neodymium selenide samples ($\text{NdSe}_{1.47}$). The error bar on the sample annealed for 5 months represents the variation in Seebeck coefficient found in seven individual measurements on the same sample.

Figure 15: Room temperature power factor versus annealing time for the lanthanum selenide samples (labeled in the legend of the plot).

Figure 16: Room temperature power factor versus annealing time for the neodymium selenide samples ($\text{NdSe}_{1.47}$).

promising material for use as a high temperature thermoelectric.

High Temperature Electrical Resistivity

The plots of the high temperature resistivities of lanthanum and neodymium selenide samples taken before any annealing had taken place can be seen in Figures 17 and 18, respectively. The increase in resistivity with increasing temperature shown in these plots indicate that these materials have a metallic type conduction.

Resistivity in materials consists of two temperature dependent factors and one temperature independent factor (equation 6 from Part I of this thesis).⁴⁴ The only temperature dependent factor that is operative in these materials above room temperature is due to the interactions between current carriers and lattice vibrations. This means that as the temperature is raised, the current carriers are scattered by the increased lattice vibration from the increased thermal energy, increasing the electrical resistivity with temperature. This explanation applies for the $\text{LaSe}_{1.47}$ throughout the entire temperature range of measurements, as seen in Figure 17 by the steady increase in resistivity throughout the temperature range (25°C to 1000°C).

The $\text{NdSe}_{1.47}$ shows a variation from this at high temperatures. The electrical resistivity for the neodymium selenide sample reaches a maximum at around 950°C, after which the resistivity values decrease, which is different from the $\text{LaSe}_{1.47}$ results. This is most probably the result of intrinsic conduction,⁴⁹ because there are no foreign dopants to donate electrically active electrons. This decrease is a result of the excitation of electrons, leaving electron holes in the valence band. The onset of this type of electrical conduction is of great detriment to high temperature thermoelectric properties. The increase in carrier concentrations causes a significant decrease in the Seebeck coefficient.

The thermal conductivity is also increased due to the ambipolar contribution from the diffusion of electron/hole pairs from the higher temperature end of the material to the

Figure 17: Resistivity versus temperature for an as hot pressed lanthanum selenide sample ($\text{LaSe}_{1.47}$).

Figure 18: Resistivity versus temperature for an as hot pressed neodymium selenide sample (NdSe_{1.47}).

cooler end. This behavior might limit the service temperature over which the neodymium selenide will be usable.

High Temperature Seebeck Coefficient

The high temperature Seebeck coefficient data for the lanthanum and neodymium selenide samples can be seen in Figures 19 and 20, respectively. The values of the Seebeck coefficient increase approximately linearly with temperature, once again showing that these materials are n-type semiconductors with metallic type conduction. This linear relationship deviates at high temperatures, at least in the lanthanum selenide material, where the Seebeck coefficient seems to level off at about 900°C. This indicates an increase in carrier concentration. This might be attributable to intrinsic conduction, but it is strange that the resistivity curve showed no indication of it. The neodymium selenide sample shows a deviation from linearity at a much lower temperature. This deviation is relatively small and gradual, so I would not think that this is due to intrinsic conduction. It is also strange that the Seebeck coefficient does not show the a peak at approximately 950 °C that is observed in the resistivity. Additional high temperature data will needed to verify these apparent anomalies at high temperatures.

High Temperature Power Factor

The high temperature power factors (S^2/ρ) of the lanthanum and neodymium selenide samples were calculated from their resistivities and Seebeck coefficients. Plots of the calculated power factors versus temperature can be seen in Figures 21 and 22, respectively. $\text{LaSe}_{1.47}$ (Figure 21) shows a nice linear increase in power factor until about 850°C, when the curve begins to curve downwards. It manages to reach a power factor of $5.36 \mu\text{W}/\text{cm} \cdot ^\circ\text{C}^2$, which would make it a promising high temperature thermoelectric material, accept for the formation of the β -phase. The power factor curve for the neodymium sesquiselenide sample peaks at $1.49 \mu\text{W}/\text{cm} \cdot ^\circ\text{C}^2$ at a temperature of

Figure 19: Seebeck coefficient versus temperature for the as hot pressed lanthanum selenide sample ($\text{LaSe}_{1.47}$).

Figure 20: Seebeck coefficient versus temperature for the as hot pressed neodymium selenide ($\text{NdSe}_{1.47}$).

Figure 21: Power factor versus temperature for the as hot pressed lanthanum selenide sample ($\text{LaSe}_{1.47}$).

Figure 22: Power factor versus temperature for the as hot pressed neodymium selenide ($\text{NdSe}_{1.47}$).

about 500°C, it then decreases to $1.17\mu\text{W}/\text{cm}\cdot^\circ\text{C}^2$ at 900°C and then it begins to curve upwards. This is not encouraging for use as a high temperature thermoelectric material. The erratic behavior of this material's power factor might just be due to the sample tested, because room temperature values of power factor for other neodymium selenides in my study exceeded $1.5\mu\text{W}/\text{cm}\cdot^\circ\text{C}^2$. As more high temperature data becomes available, it will be more apparent whether or not the neodymium selenide is not a good thermoelectric material, or whether there was a problem with the sample tested.

The evidence obtained in this study shows both the lanthanum and neodymium selenide as promising thermoelectric materials. The lanthanum sesquiselenide has initially excellent properties at high temperatures, but the γ -phase Th_3P_4 cubic defect structure transforms to the β -phase tetragonal structure at high temperatures in the presence of an extremely small amount of oxygen, which slowly destroy the outstanding thermoelectric properties of $\text{LaSe}_{1.47}$. This study indicates that it would take a long time for the sample to transform to more than 20% β -phase, but when one considers that the space missions last a decade or more, the LaSe_x material is not acceptable for this application. The γ -phase of the neodymium sesquiselenide shows very promising stability at high temperatures for long periods of time, but with a power factor of no greater than $1.5\mu\text{W}/\text{cm}\cdot^\circ\text{C}^2$ at high temperatures, it is not very encouraging. This will be better known when more data is available.

GENERAL CONCLUSIONS

From the data given in Part I of this thesis, I believe that it can be safely concluded that yttrium sesquisulfide is not a viable candidate for a high temperature thermoelectric material, at least not when mechanically alloyed with copper boron or aluminum. The materials alloyed with copper and boron were insulators, and of no use. The materials alloyed with aluminum, although their behavior is interesting, and is largely unexplained to this point, had power factors that were far too small for the material to be of any practical use. In addition, there is the problem that this material becomes an insulator after heat treatment at high temperatures, which makes it particularly ill equipped for high temperature applications. It may be worth while to further investigate the properties of the yttrium sulfide alloyed with aluminum in order to answer some questions not answered in this study, but its use as a high temperature thermoelectric material can be ruled out.

Of the materials studied in Part II of this thesis, the lanthanum selenide shows very promising properties for use as a high temperature thermoelectric material. The only problem is the appearance of the tetragonal oxide β -phase with the smallest presence of oxygen, which was also reported by Besancon et al,²⁹ destroys these properties. Despite the fact that this study shows that the γ to β transformation happens slowly, it still would limit the useful life of a radioisotope thermoelectric generator, which, for space power applications whose mission durations are measured in the decades, is unacceptable. As for the neodymium selenide, the absence of the γ to β transformation, even after 6 months at 1000°C, makes this material a good prospect for use as a high temperature thermoelectric material. It is true that the power factors for this material attained in this study are too low to be very useful, however, others have found much more encouraging results.⁵¹ Neodymium selenide (NdSe_x where $x = 1.45$ to 1.50) shows a strong potential for use as a high temperature thermoelectric material.

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