MIXING METALS FOR MAGIC MATERIALS: Analysis of Binary Eutectic Alloys for Metamaterial Applications

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George M. Pharr, Major Professor

We have read this thesis and recommend its acceptance:

Claudia J. Rawn, Erik G. Herbert

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Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
MIXING METALS FOR MAGIC MATERIALS:  
Analysis of Binary Eutectic Alloys for Metamaterial Applications

A Thesis Presented for the  
Master of Science  
Degree  
The University of Tennessee, Knoxville

Ethan Elder Fox  
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ABSTRACT

Uses of metamaterials, also known as negative index materials (NIMs), are wide ranging and include lenses that have a resolution beyond the diffraction limit, incredibly small antenna, and cloaking devices for optical, infrared, and microwave wavelengths.

The unique properties of metamaterials are not found in any naturally occurring material. By having simultaneously negative values for $\varepsilon$ [electrical permittivity] and $\mu$ [magnetic permeability], a metamaterial can have a negative index of refraction over a certain frequency band. The unique properties of negative index materials emerge chiefly from their highly ordered structure.

Binary eutectic alloys have the potential to be used as a metamaterial if their intrinsic material properties are properly selected and the eutectic has the proper microstructure. The eutectic microstructures of interest for this work are the lamellar structure, with one phase being electrically conducting and the other phase being insulating or semiconducting, and rod microstructure with conducting rods in an insulating or semiconducting matrix.
The use of directional solidification of a eutectic alloy in order to create the highly ordered structure necessary for a metamaterial is a new frontier. The selection of an appropriate alloy for this application is the purpose of this work.

Two classes of materials were investigated: conducting metal + rare earths and semiconductor + conducting metal. Oxidation of the rare earths can form the necessary insulating layer. Eutectic alloys were created in an arc melter and analyzed using metallography and electron dispersive x-ray spectroscopy.

While compounds with rare earths can provide needed properties, preventing oxidation of the rare earths long enough to allow good mixing with the conducting metal proved difficult. Germanium with 9.2 at% titanium seems a good candidate based on structure as it forms conducting rods in a matrix of primarily germanium. Silver with 10 at% lanthanum forms a lamellar structure and has a highly conducting phase layered with a phase that has the potential to become insulating.

Future work should involve directional solidification of a eutectic alloy to further investigate its potential as a metamaterial.
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CHAPTER I

INTRODUCTION

Metamaterials

Not found in nature, metamaterials are a class of artificial media with an ability to effect electromagnetic (EM) radiation in unusual ways. Having simultaneously negative values of electrical permittivity, $\varepsilon$, and magnetic permeability, $\mu$, over the same frequency range, metamaterials can have a negative index of refraction [1]. The effects of negative $\mu$ and $\varepsilon$ were first proposed by Vesalago in 1964, though the first demonstration of a metamaterial did not occur until the year 2000 [2][3]. Figure 1 shows the difference between what happens when an incident EM ray strikes a conventional material and a metamaterial. The left (white) side of Figure 1 can be thought of as some conventional material or a vacuum. The right (gray) side of the figure shows how an EM ray is refracted depending on whether the material in question is conventional material (upper right) or negative index material (lower right).

Uses of metamaterials, also known as negative index materials (NIMs), vary widely and include everything from ultra-small antennas [4], absorbers to increase the efficiency of photovoltaics, superlenses which can see beyond the diffraction limit of conventional lenses, seismic protection for buildings and even electromagnetic cloaking, including optical cloaking [1][5].
Figure 1. NIM refraction vs. conventional material refraction. Diagram comparing what happens to an EM ray when it strikes a conventional material versus a negative index material.
Metamaterial construction is analogous to that of conventional matter in that the properties of some regular bulk materials owe their properties not only to the atoms with which that material is made, but also to how those atoms are arranged and how they interact with each other. Negative index materials can be thought of as being composed of “meta-atoms” which are stacked together in a highly ordered manner, similar to a crystal lattice, Figure 2 illustrates this concept [6]. These individual meta-atoms can have a variety of forms including an array of thin wires, tightly wound sheets (chiral arrangement), two concentric C-shaped rings called split-ring resonators and many more [5].

Construction techniques for metamaterials vary depending on the scale of the individual elements. Etching alloys for components can be used at the millimeter scale while advanced lithography alloys are required for the dimensions to be reduced to nanometers [6].

An important aspect to consider is that the size of the aforementioned meta-atoms scales with the wavelength of the radiation they are intended to effect and that the meta-atoms may need to be up to one order of magnitude smaller in size than that wavelength [1] [7]. This adds to the difficulty of fabrication of optical metamaterials as optical wavelengths are between approximately 400 and 700 nanometers.
Figure 2. Periodic concept of metamaterials. This diagram helps to illustrate the periodic array concept of metamaterials and how it relates to conventional materials. Clockwise from top right: stacked split ring resonators (SRR), chiral, left-handed transmission line, varicap SRR, terahertz absorber, varicap diode, and double SRR [1].
Eutectics

Binary eutectic alloys have promise for use as metamaterials. A binary eutectic alloy is a homogeneous mix of two distinct phases. Here, two pure elements are combined and result in an intermetallic phase composed of the two elements in a known stoichiometry and the other phase is primarily one element with a finite amount of the other element dissolved in it [8]. A simple representation of a binary phase diagram is given in Figure 3.

The architecture of how these two phases arrange themselves can be quite varied though there are two types that are of importance in for this work. The first is a lamellar structure in which the two phases form alternating layers, one on top of the other. The second is a rod structure in which cylinders of one phase are embedded in a matrix of the other phase. Figure 4 shows a side-by-side schematic of both lamellar and rod eutectics.

Rod eutectics tend to form when the volume fraction of one phase is 0.3 or less with the rods consisting of the minority phase. Lamella tend to form when the volume fraction of one phase is between 0.3 and 0.7, as seen in Figure 5 [8].
Figure 3. Representative binary phase diagram. The eutectic point is at composition $X_E$.

At point $X_E$ the liquid solidifies to form a homogeneous mixture of $\alpha$ and $\beta$ phases.
Figure 4. Lamellar vs. rod eutectic. A schematic of (a) lamellar eutectic growth and (b) rod eutectic growth. [9]
Figure 5. Expected eutectic microstructure based on volume fraction. This plot shows the expected microstructure (lamella or rods) based on the relationship between phase volume fraction and stored energy density ratio, \( R \), where \( \varepsilon \) is the interface energy per unit volume. The solid and dashed lines indicate when the rods will have a hexagonal or square array respectively [8].
Physical, electromagnetic and optical properties of eutectics can be as varied as the elements of which they are comprised. Here, it is most desirable for one phase of the eutectic to be electrically conductive while the other is insulating or semiconducting. For the lamellar structure, the layers should alternate between being electrically conducting and either electrically insulating or semiconducting. In the case of a rod eutectic, it is desirable to have conducting rods inside a matrix of material that is either insulating or semiconducting. Additionally, in the event of conducting rods inside a matrix with undesirable properties, the matrix can possibly be etched away allowing air to act as the necessary insulator.

**Directional Solidification**

While research into metamaterials has been undertaken for several years, use of a eutectic alloy in combination with directional solidification is a new frontier. Directional solidification in its various forms is a technique for achieving fine control over the microstructure of crystalline materials [10] and can be used to achieve the high precision microstructure needed to use a eutectic as a metamaterial. Selection of an alloy that can be directionally solidified using the Bridgman technique is the end goal of this work.

The Bridgman method involves a cylindrical crucible of molten material that is drawn out of a heated zone and into a cooled zone as seen schematically in Figure 6. This technique allows for control over the temperature differential
between the hot and cold zones and the withdraw rate. Note that Fig. 6 shows a ‘chilled plate’ rather than the chilled zone that would actually be used. The use of a seed crystal allows the orientation of the final crystal to be pre-selected [8].

Furthermore, it has been well documented that proper control over the solidification rate can transform a eutectic alloy that tends to form lamella into one with a rod structure [11][12][13]. This is potentially advantageous for a eutectic with necessary phase properties but with a lamellar structure when a rod structure is more desirable.

![Figure 6](image-url)

**Figure 6.** Bridgman solidification technique. A crucible of material is melted in a heated zone and slowly drawn down out of the heated zone allowing it to solidify at a controlled rate. [8]
CHAPTER II
MATERIALS AND METHODS

Materials Overview

A variety of alloys were considered for the metamaterial application. Silver based alloys offer some promise due to silver having the highest electrical conductivity of any metal. In a review of the binary phase diagrams of silver alloys, several candidates were identified as worthy of further investigation. These included Ag-Si, Ag-Ce, Ag-Er, Ag-Dy, Ag-La and Ag-Y. Some criteria for initial selection included presence of a well defined eutectic point, availability of alloying elements, and ease of working with the alloying elements (e.g., compounds that react violently with air were not considered).

Two copper based alloys, chosen for the same reasons as the silver based alloys, were also investigated. The alloys are copper-lanthanum and copper-cerium. Both alloys tend to form copper rods in a copper + rare-earth matrix [14].

Three germanium based alloys were investigated after much work on silver alloys was finished. These eutectics were Ge-Ti, Ge-Ni and Ge-Co. Germanium, nickel, cobalt, and titanium are all relatively stable in air, unlike the rare earths used in the silver and copper based alloys.
Alloys studied in this work, along with the atomic percent of the phases present and electrical resistivity (if known), can be found in Table 1.

Some additional alloys were prepared and investigated, however, they either had severe drawbacks that were found or it became apparent that their study would not yield useful information. The alloys in question are Ag-81.0at%Ce, Ag-76.5at%La, Ag-0.9at%Dy, Ag-2.0at%Er, Ge-33.3at%Co, Ge-50.0at%Ni and Ge-33.3at%Ti. Details on each of these alloys can be found in the appendix.

**Methods Overview**

Arc melting was exclusively used to combine the raw metals into a single button useful for further study. The machine used for this research was a Edmund Bühler MAM-1 with a water cooled, copper crucible. The air in the unit was evacuated and high-purity argon was used to backfill the chamber to 600-700 torr. A zirconium getter was used to absorb any oxygen left in the chamber after evacuation and backfilling with argon.

Buttons were flipped and remelted at least seven times to ensure good mixing. Some alloys were reluctant to mix and were flipped and remelted up to 15 times. The number of times each button was flipped and remelted is noted in each individual alloy’s section.
<table>
<thead>
<tr>
<th>Metal [Intermetallic] [Matrix w/ solubility]</th>
<th>Atomic Percent</th>
<th>Electrical Resistivity (Ohm-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-10.0at%Ce</td>
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<td></td>
</tr>
<tr>
<td>Ag4Ce</td>
<td>49.9</td>
<td></td>
</tr>
<tr>
<td>Ag-0.05at%Ce</td>
<td>50.1</td>
<td></td>
</tr>
<tr>
<td>Ag12Ce</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag-11.8at%Dy</td>
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<td></td>
</tr>
<tr>
<td>Ag51Dy14</td>
<td>51.7</td>
<td></td>
</tr>
<tr>
<td>Ag-1.3at%Dy</td>
<td>48.3</td>
<td></td>
</tr>
<tr>
<td>Ag-11.5at%Er</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag51Er14</td>
<td>44.9</td>
<td></td>
</tr>
<tr>
<td>Ag-3.6at%Er</td>
<td>55.1</td>
<td></td>
</tr>
<tr>
<td>Ag12Er14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag-10.0at%La</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag5La</td>
<td>59.7</td>
<td></td>
</tr>
<tr>
<td>Ag-0.05at%La</td>
<td>40.3</td>
<td>1.65x10^-8</td>
</tr>
<tr>
<td>Cu-11.5at%Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu51Y14</td>
<td>50.5</td>
<td></td>
</tr>
<tr>
<td>Cu-1.31at%Y</td>
<td>49.5</td>
<td></td>
</tr>
<tr>
<td>Cu-9at%Ce</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu6Ce</td>
<td>63.4</td>
<td>72x10^-8</td>
</tr>
<tr>
<td>Cu~0at%Ce</td>
<td>36.6</td>
<td></td>
</tr>
<tr>
<td>Cu-9at%La</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu6La</td>
<td>63.4</td>
<td>40x10^-8</td>
</tr>
<tr>
<td>Cu~0at%La</td>
<td>36.3</td>
<td></td>
</tr>
<tr>
<td>Ge-27at%Co</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge2Co</td>
<td>83.6</td>
<td>1.4x10^-6</td>
</tr>
<tr>
<td>Ge~0at%Co</td>
<td>16.4</td>
<td>~0.3</td>
</tr>
<tr>
<td>Ge-33at%Ni</td>
<td></td>
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<tr>
<td>GeNi</td>
<td>65.4</td>
<td></td>
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<tr>
<td>Ge~0at%Ni</td>
<td>34.6</td>
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<tr>
<td>Ge-9.2at%Ti</td>
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<tr>
<td>Ge2Ti</td>
<td>22.5</td>
<td>2.10x10^-4</td>
</tr>
<tr>
<td>Ge-2.2at%Ti</td>
<td>77.5</td>
<td></td>
</tr>
</tbody>
</table>
After cooling fully the buttons were sectioned with a slow speed diamond saw and mounted in two-part epoxy. Two different cut orientations were used, particularly for the silver based alloys, and are diagramed in Figure 7. Axial cuts are vertical so the visible surface area is viewed as if looking horizontal through the sample relative to the button when it was created in the arc melter. Radial cuts are made in the horizontal plane to the surface is seen as if looking down on the sample.

![Diagram showing cut orientations]

Figure 7. Cut orientation diagram. This diagram shows the two primary cut orientations used particularly for the silver alloys.

All of the alloys that were investigated were cut into two or more pieces and polished through 1200 grit sandpaper with running water. Samples that did not seem to react adversely with water were then polished with 0.5 micron alumina in
a Vibromet vibratory polisher followed by polishing in colloidal silica in a similar Vibromet polisher. Polishing times varied depending on how quickly each sample achieved a satisfactory level of visibility under an optical microscope. Alloys that reacted poorly in water, in particular the rare-earth dominant samples were hand polished on a felt wheel with 0.1 micron diamond and oil suspension then rinsed thoroughly in methanol. This step produced a visible microstructure without the severe oxidation observed when polished in a Vibromet with water and polishing media.

Methods of investigation included optical microscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). Optical microscopy is an obvious first step for inspecting the microstructure of the alloys.

Depending on the alloy, the microstructure may not have been visible and optical inspection was useful only to insure the surface was well polished. The next technique used to view the surface was an SEM which has a much higher resolving power.

Energy dispersive X-ray spectroscopy (EDS) in the SEM was used primarily to identify the two phases of the microstructure within a given alloy. It was also used to identify the primary phases present in the cases where the correct composition was not achieved. It should be noted that some of the
microstructural features analyzed with EDS were quite small and on the order of the interaction volume of the electron beam with the material. Also, there is no certain way to know what is under the surface of the as cast microstructure and whether the feature being sampled is uniform to the depth reached by the interaction volume. Despite these sources of error, EDS remained a useful tool to gain insight into the composition of the material at hand.

**Materials Investigated**

*Silver Base Alloys*

**Ag-10.0at%Ce**

Initially, there was an error in conversion from atomic percent to weight percent for the creation of a silver and cerium button, but once that was corrected, the process went more smoothly. Two eutectics were created with these two elements with the first being Ag-10at%Ce, seen on the left side of the phase diagram in Figure 8. The second is the far right eutectic point for which details can be found in Appendix A. A small amount of evaporation occurred, 5.00 g raw material in and a 4.94 g button out, a 0.01% weight loss. Silver has a higher vapor pressure than cerium so it is reasonable to assume the weight loss was due to silver evaporation.
**Ag-12.0at%Dy**

Of the four eutectics that exist on the silver-dysprosium phase diagram, seen in Figure 9, the composition used for this section was Ag-12.0at%Dy. The solubility of dysprosium in silver is relatively low at 1.3%, and the intermetallic phase has the composition of Ag$_{51}$Dy$_{14}$.

Directional solidification requires any alloy to be cast into a cylindrical mold placed in the Bridgman Furnace. This was one of the first samples to be created for this research, and there was a desire to drop cast the 5g button into a small mold and then be sectioned and polished. Drop casting was performed in the mini arc melter described previously using a water cooled copper mold with mold dimensions 35mm long and 4mm diameter. Surface tension of this alloy was such that a small vacuum had to be applied to pull the molten metal into the mold.

Successful drop casting took several attempts to get right, and once that was done, the small ingot was sectioned into two pieces; one cut was in the radial direction of the ingot and the other was in the axial direction.

Initial work with Ag-Dy showed a primary phase of dysprosium when polished and inspected optically. Even though great care was taken to ensure the proper ratio of materials was weighed out, there was still some small amount of weight loss in the initial alloy amounting to 0.02g or 0.4 percent. The vapor pressure of
silver is somewhat higher than that of dysprosium so most likely the weight loss came from evaporation of silver though some dysprosium may have also evaporated.

**Ag-11.8at%Dy**

After finding a non-trivial amount of primary phase in the button created from the literature eutectic ratio, a second button was created with a slightly decreased amount of dysprosium. The two base elements were melted together in a mini arc melter and flipped and remelted seven times to ensure good mixing. The button was sectioned, mounted and polished by hand through 1200 grit sandpaper, polished for 4 hours with 0.5 micron alumina in a Vibromet vibratory polisher followed by 24 hours in another vibratory polisher with colloidal silica.

**Ag-11.5at%Er**

Following the creation of a silver and dysprosium button, an alloy of silver and erbium of was created. The eutectic point for this alloy is Ag-11.5at%Er, as shown on the far left side of the phase diagram in Figure 10. The solubility of erbium in silver at 3.6 atomic percent is quite high relative to the other compounds studied.
Figure 8. Silver-cerium phase diagram [15].
Figure 9. Silver-dysprosium phase diagram [16].
Figure 10. Silver-erbium phase diagram [17].
Weight losses in the creation of the silver-erbium button were not observed. Polishing did not yield a microstructure that was very clear under an optical microscope. SEM images provided a somewhat clearer picture.

**Ag-10.0at%La**

Silver and lanthanum combined at Ag-10.0at%La is one of the more promising alloys. Lanthanum’s solubility in silver is very low at 0.05 atomic percent, thus having minimal effect on the conductivity of silver. The phase diagram for silver-lanthanum is given in Figure 11.

**Ag-11.5at%Y**

Yttrium was alloyed with silver at its eutectic of Ag-11.5at%Y. Figure 12 shows the binary phase diagram of these two metals. Weight losses in the making of this alloy were on the order of 1.6% and were most likely from the yttrium due to its higher vapor pressure. The button was sectioned and mounted as discussed previously.
Figure 11. Silver-lanthanum phase diagram [18].
Figure 12. Silver-yttrium phase diagram [19].
Copper Based Alloys

Cu-9.0at%Ce

After the two unsuccessful attempts to create a well-mixed copper-cerium, a third attempt was made with somewhat more success. The eutectic point in question is Cu-9.0at%Ce as shown in Figure 13. A mini arc melter was used. The goal weight for this button was 4 grams and losses were approximately 3 weight percent. To ensure better mixing than the initial alloying attempts the button was melted and flipped 15 times. A dark gray oxide layer formed on the outside of the button in the final few melts. This dark gray oxide layer was more apparent upon sectioning in that bright, shiny copper was found in the interior and there was a matte gray layer surrounding that on the outside. A mounted specimen was hand polished through 1200 grit sandpaper under running water.

Cu-9.0at%La

A 4 gram button of Cu-9.0at%La was the goal, and weight losses were 1.2 percent after melting and flipping the button 15 times to ensure good mixing. Similar to the copper-lanthanum eutectic in the previous section, a matte gray oxide layer formed on the outside of the button in the final few flips. After cutting the button into 2 pieces, it appeared that the 2 metals mixed well enough that there was no oxidized, unmixed rare earth in the interior. However, as with the Cu-9.0at%La button, there was a layer of matte gray oxide enveloping the shiny
copper-lanthanum eutectic bulk. A phase diagram for copper and lanthanum is given in Figure 14.

**Germanium Base Alloys**

**Ge-27at%Co**

Cobalt forms one of two eutectics with germanium at the composition Ge~27at%Co, see Figure 15. Losses in the creation of a 5 gram button were greater than for the other germanium compounds and also for the silver based alloys and were on the order of 3.5 percent. The button was sectioned, mounted in epoxy, and hand polished through 1200 grit sandpaper under running water; following this, the sample spent four hours in a vibratory polisher with 0.5 micron alumina and another four hours in a vibratory polisher with colloidal silica.

A second button with a weight of 4 grams was created under the same circumstances as the previous button and then mounted and polished under the same conditions. Weight losses were negligible. A 4 gram button was created as opposed to a 5 gram button due to difficulty of getting 5 grams of material into the small copper crucible of the mini arc melter.
Figure 13. Copper-cerium phase diagram [20].
Figure 14. Copper-lanthanum phase diagram [21].
Figure 15. Germanium-cobalt phase diagram [22]
**Ge-33.3at%Ni**

The first germanium-nickel eutectic is at the composition Ge-33at%Ni with the intermetallic of GeNi and a germanium phase with negligible dissolved nickel. Figure 16 shows the germanium-nickel phase diagram. Losses for this first button were less than 0.3 percent.

Four gram buttons were made for this and subsequent alloys as the density of germanium and the alloying metals is less than that of silver or copper and it’s alloying elements and the amount of material needed to create a 5 gram button tends to be more than the small arc melter crucible can reasonably hold.

**Ge-9.2at%Ti**

This germanium alloy is one with the addition of titanium at the eutectic point of Ge-9.2at%Ti. See Figure 17 for the phase diagram of germanium and titanium. Weight losses were small, on the order of 2%, for the 5 gram button. It should be noted that care was taken to prevent chipping of germanium under the arc by placing the germanium in the bottom of the crucible with the titanium on top, and the arc was struck at the lowest power and slow increased in intensity as the metals heated and began to melt.
Figure 16. Germanium-nickel phase diagram [23].
Figure 17. Germanium-titanium phase diagram [24].
CHAPTER III
RESULTS AND DISCUSSION

Silver Based Alloys

Ag-10.0at%Ce

Upon sectioning and inspection with an optical microscope it became apparent that the Ag-10at%Ce specimen was very near the eutectic composition and there was only a small amount of noticeable primary phase. Micrographs are shown in Figure 18. The darkly colored primary phase was grouped on the bottom of the sample nearest the edge contacting crucible and was evident to 20 microns from the edge of the specimen.

The microstructure of this eutectic is lamellar with the noticeable addition of a large amount of layered stripes present throughout the sample. The stripes seem to consistently be composed of seven layers; the outside layers are light in color and lamella branch off from this layer. The light outside layer is followed by a thick dark layer, a thin layer of light color, and a very thin dark layer in the center; continuing across the stripe is a mirror image with the appearance mentioned the previous sentences. The lengths of these stripes vary from approximately 10-100 microns and have a width between 1-2 microns.
A second variety of stripe is also apparent under magnification. These stripes have a varying number of layers from 12-22 with a length and width from 5-15 microns and 10-50 microns respectively. As with the longer, thinner stripes previously described, these anomalies alternate light and dark layers with the lighter layer being approximately half the width of the dark layers.

EDS data indicated that the lamellar structure is close to nominal composition with approximately 10 atomic percent cerium present in the areas analyzed. Lighter areas are the silver solid solution (0.05 at% cerium) and darker areas are the intermetallic, Ag₄Ce.

In general, the eutectic microstructure observed here is similar to that seen by others such as Stapf and Jehn in their examination [25].

![Figure 18. Ag-10.0at%Ce micrograph. (a) Micrograph showing a small amount of primary phase along with the lamellar eutectic. The dark area on the lower right edge is the mounting epoxy. (b) Thick lamellar stripes seen towards the middle of the sample.](image-url)
**Ag-12.0at%Dy**

Dysprosium has an advantage over the other rare earths used for this research in that it is relatively stable in air.

As seen in Figure 19, this alloy takes on primarily a lamellar structure. However, SEM images reveal the presence of what appears to be rod-like structures (see Figure 19b). Optical microscopy revealed a primary phase despite there being negligible weight losses in this specimen. An interesting aspect of this primary phase is that most, but not all, of the discrete areas of the phase are hexagonal and have a portion of eutectic inside a circular break in the middle. These structures appear in both the radial and axial sections of this alloy.

![Figure 19. Ag-Dy micrograph. (a) A 100x optical images of Ag-12.0at%Dy showing some primary phase along with the lamellar eutectic structure. (b) An SEM image of Ag-11.8at%Dy showing what appears to be rods along with lamellar structure.](image-url)
**Ag-11.8at%Dy**

Due to the darker color of the primary phase seen in the Ag-12.0at%Dy discussed in the previous section, it was hypothesized that there was an excess amount of dysprosium. To test this, another sample was prepared with 0.2 percentage points less of the rare earth, i.e. Ag-11.8at%Dy. The sample was inspected under an optical microscope and found to consist of a lamellar and rod structure without the dark, six sided areas seen in the Ag-12at%Dy sample, see the comparison between the two aforementioned silver-dysprosium alloys in Figure 19. This calls into question the literature eutectic. The true eutectic appears to be closer to the 11.8 at% dysprosium.

**Ag-11.5at%Er**

Silver and erbium produce a lamellar eutectic that is difficult to see clearly with an optical microscope but is visible with an SEM. There are significant differences in what is seen in this sample depending on whether the radial or axial sectioning specimen is viewed. Figure 20 shows a comparison of the radial and axial sections. The radial section has a fairly clear lamellar structure. The axial section, however, appears to be cratered with holes and there is no clear microstructure whatsoever. Even with the advantage of depth of field provided by the SEM it is not clear whether these dark spots are holes or if they are cross sections of rods. It should be noted that these images were taken based on the
same sample, the only difference being the orientation in which the images were taken; both were polished at the same time and under the same conditions.

![Figure 20](image)

**Figure 20.** Ag-11.5at\%Er micrograph. (a) Radial cut section of silver-erbium showing lamellar structure. (b) Axial cut section showing what appears to holes or pitting. Both specimens were cut from the same button and were polished under the same conditions.

Also, note that the scale of both micrographs is the same.

**Ag-10.0at\%La**

A silver dominant eutectic with lanthanum has the desirable property of having a low solubility of lanthanum in the silver matrix at 0.05 atomic percent. This solid solution has an electrical resistivity of 16.5 nOhm-meters, which is only slightly higher than the 16.0 nOhm-meters of pure silver [26]. The structure of the as-cast alloy appears very similar in both the radially and axially cut samples in that both have a clear lamellar structure with the addition of long, multi layered stripes. Figure 21 has micrographs for both radial and axial sections. These stripes alternate dark/light with the internal layers running the length of the stripe.
as a whole. The internal layers have a similar width and the number of layers per stripe varies from 3-8 in the SEM images taken. The width of the stripes is approximately 0.5 – 1.5 microns and the length varies from 2-30 microns.

![Figure 21. Ag-10.0at%La micrograph. (a) Axial sectioning and (b) radial sectioning show a similar microstructure.](image)

Data from EDS varied depending on where the scan was taken with values ranging from 8 to 13 atomic percent lanthanum. There is no apparent variability in microstructure of the sample so this variance may be attributed to chance selection of where the scan was taken. The dark areas are the silver-lanthanum intermetallic, Ag₅La, while the light areas are the silver dominant solid solution. EDS data was taken at several locations, both dark and light colored, though the data should be taken as qualitative rather than quantitative due to the size of the areas scanned being smaller than the interaction volume of the system.
Additionally there is no way to know of what is below the visible surface of the sample.

A very small number of dark particles were seen during microscopy. These appear to be oxidized lanthanum.

**Ag-11.5at%Y**

The eutectic of silver and yttrium has a primarily lamellar microstructure with some sections that appear to be entirely rod structures with the rods being approximately 1 micron in diameter. Sections of rods and lamella can be seen in Figure 22 and are spread throughout the button and do not seem to show a preference for cut orientation.

![Figure 22. Ag-11.5at%Y micrograph. (a) Shows a combination of lamella, rod and a small amount of primary phase. (b) A closer view of the rod structure.](image)
Based on EDS data the dark areas of the micrograph are silver-yttrium intermetallic, Ag$_{51}$Y$_{14}$, while the lighter colored areas are silver solid solution. As previously mentioned for other samples the areas analyzed were smaller than the interaction volume of the EDS system so the data should be taken as qualitative instead of quantitative.

**Copper Based Alloys**

**Cu-9.0at%Ce**

Initial attempts to mix a copper and cerium eutectic were unsuccessful due to oxidation of the cerium. A final attempt to mix the two materials appeared to work in that upon sectioning of the 4.0 gram button there was no apparent unmixed material present, so the alloy was polished and investigated further. After polishing, the sample appeared smooth and without scratches under an optical microscope, yet the microstructure was still difficult to discern. Using an SEM did not improve the visibility of the microstructure. Etching may have improved the ability to see features on the polished surface; however a simpler solution was devised. Cerium oxidized quickly in hot water so the mounted sample was placed in a beaker of hot tap water for one hour and then placed in an optical microscope. Micrographs are found below in Figure 23.
Figure 23. Cu-9.0at\%Ce micrograph. (a) Shows the lamellar structure of this alloy. (b) Clearly seen are specks of oxidized cerium that did not fully mix with the copper.

With the visibility of the microstructure improved significantly, an optical microscope was powerful enough to see features of the surface. Despite the button being melted and flipped 15 times, it appears the two metals did not fully mix. The section that was viewed was speckled with many small spots on the order of 1 micron of what appears to be oxidized cerium –due to its dark gray color—along with several long stripes in the interior of the sample and also areas on the outside of the sample –the region exposed to the atmosphere of the arc melter.

The areas other than the dark oxidized portions are primarily lamellar with a few large areas with a rod structure near the portion of the button that was highest when it was cast. The eutectic area with the lamella structure also appears to have a granular aspect to its appearance. There is an alternating dark-light
stripe appearance inside each so-called grain while there is also a difference in tone between each grain while each one still has the same lamella structure. Pure copper has a similar grain structure when sectioned and polished.

**Cu-9.0at%La**

Visibility of the microstructure of this alloy was improved in exactly the same way as with the Cu-9.0at%Ce eutectic, that is, with hot water.

The transition metal dominant eutectic of copper and lanthanum suffers a similar issue with mixing of the two materials as does the copper and cerium eutectic. The small specks of dark gray material tend to be rectangular in shape are on the order of 3 microns long and 1 micron wide and are present across the polished surface of this sample, see Figure 24. Also, as with the copper-cerium eutectic, there are areas of dark gray, presumably oxidized lanthanum on the outside edge of the alloy. On the interior of the alloy are a few small, irregularly shaped clumps of a higher luster than the surrounding material. These bright areas can only be primary copper. Due to some cerium remaining unmixed, the composition was effectively shifted to a hypoeutectic one causing primary copper to solidify first. The remainder of the microstructure consists of sections of either lamella or rods spread across the surface of the specimen.
Figure 24. Cu-9.0at%La micrograph. Seen within the lamellar structure of this micrograph are unmixed bits of lanthanum and light areas of copper.

Others have observed as-cast Cu-9.0at%La to form a rod structure without any reported lamella [27]. Any observed lamella in the eutectic portion of the specimen are likely to be a section of rods that are oriented with their long axis in plane with the cut of the button.

Germanium Based Alloys

Ge-27at%Co

The two phases of the eutectic are germanium with negligible amounts of dissolved cobalt and an intermetallic of the stoichiometry Ge$_2$Co. Questions arose about the microstructure of the first button created which prompted the creation of a second button to confirm the first button had the correct ratio of germanium to cobalt. Microstructures seen in both specimens are very similar
Much of the visible area is taken up by a lamellar structure. The lamella areas have the appearance of having been etched even though the last step was polishing in colloidal silica in a vibratory polisher.

The remainder of the micrograph in Figure 25 consists of stripes of plain material between 100 and 300 microns long and 10-30 microns wide. The stripes have minimal texture compared to the lamella. There are some thin striations present on the stripes that have a similar appearance to ripples in sand created by surf on a beach.

Figure 25. Ge-27at%Co micrograph. The diagonal stripes are approximately 34at% cobalt while the other areas are approximately 29 atomic percent cobalt.

EDS data indicated that the flat, wide stripes are on the order of 35 atomic percent cobalt and 65 atomic percent germanium while the lamella are on the order of 29 atomic percent cobalt and 71 atomic percent germanium. Those
atomic percents, however, are true when only taking germanium and cobalt into account. Allowing for other elements shows 30 at% and 54 at% for cobalt and germanium respectively with the remaining 16 at% being taken up by copper. Recall a copper crucible was used to create these alloys so the presence of some copper does not come as a surprise given that the melting point of cobalt is more than 400°C higher than that of copper. However, the large amount of copper is suprising.

**Ge-33.0at%Ni**

The microstructure of germanium nickel was seen to be relatively uniform across the entire sample and had a lamellar structure with a width of less than 1 micron across each layer, see Figure 26. The only notable differences in structure are that some areas have long lamella layers and the majority of the micrograph consists of tightly bunched and coiled lamella.

The copper content for this sample was measured as approximately 4 percent on all EDS measurements. Even though copper tape was used to aid in grounding the coupon, it does not seem likely that it interfered with the EDS measurement since the copper tape was on the borders of the sample and data was taken from the middle of the sample. A copper crucible was used in the creation of all alloys and the melting point of nickel is 371°C above that of copper. Even though the
crucible was water cooled, it is still possible that some material melted and mixed with the nickel and germanium.

![Image](image.jpg)

**Figure 26. Ge-33.0at%Ni micrograph. 3000x image of the lamellar structure of Ge-Ni.**

Calculated volume fractions of the intermetallic versus germanium are 0.528 and 0.472, putting the eutectic solidly inside the domain within which a lamellar eutectic is formed. Micrographs confirm this.

**Ge-9.2at%Ti**

The eutectic of germanium-titanium has a rod microstructure. Figure 27 shows titanium rich rods protruding from the sample with cross sections from round to oval and range in width from 30 microns to around 1 micron. Other areas in between the protruding rods are smoother and have striations about 0.5 microns wide and with varying lengths.
Figure 27. Ge-9.2at%Ti micrographs. (a) Low mag SEM image showing two distinct phases. Rods with a high Ti content protrude smooth portions that are a Ge dominant solid solution. (b) Close-up of the Ti rich rods.

From EDS data, the smooth sections are the germanium solid solution and appear to contain between 2 and 4 at% titanium. The literature solubility of titanium in germanium is 2.2 at%. The rods are the intermetallic phase of Ge$_2$Ti with ~2-3 at% copper. The most plausible reason for the presence of copper in this alloy is the same as for the Ge-Co and Ge-Ni alloys as the temperature required to melt titanium is 600°C higher than that to melt copper.

Calculated volume fractions for this eutectic have the germanium phase at 0.81 and the Ge$_2$Ti comprising the remainder. The presence of rods of the minority phase come as no surprise.
CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Many of the alloys explored during this work have interesting characteristics that, individually, may be useful in the construction of a metamaterial. However, when considered on a whole, these same alloys also have several major drawbacks. The low electrical resistivity of silver and copper is desirable in the conducting phase though rare-earths are challenging to work with given how easily they oxidize before being fully mixed with conducting counterpart. Cerium or lanthanum in combination with copper were especially challenging to work with in regards to their easily oxidized nature and failure to fully mix with copper.

Despite the challenges of working with rare earths, the silver with 10at% lanthanum is the best candidate from the metal + rare earth category. There is an intermetallic phase that can oxidize and become electrically insulating along with a silver phase in which lanthanum has a very low solubility, thus having minimal negative effect on the silver conductivity.

From the semiconductor + metal category, the germanium with 9.2 at% titanium is a promising choice for a rod structure inside a semiconductor matrix. The effect on electrical conductivity of the titanium dissolved in the germanium matrix needs to be investigated.
Use of a non-copper crucible for metals with melting points significantly higher than that of copper will be necessary for future work.

Further research should involve attempting to directionally solidify the aforementioned alloys.
LIST OF REFERENCES


APPENDIX
Alloys described in this appendix were not relevant enough to be included in the main portion of the text. They either had drawbacks too severe to be considered as a metamaterial or were not studied in enough depth to provide a great deal of information.

**Rare Earth + Silver Compounds**

Two alloys of silver were created on the rare earth dominant side of their respective phase diagrams to see what might happen. These alloys show little to no promise due to the reactive nature of their primary constituent.

**Ag-81.0at%Ce**

A second button of silver cerium was created from the eutectic on the cerium-dominant side of the phase diagram with a composition of Ag-81.0at%Ce. The reasoning for this composition is the same as for the lanthanum dominant silver alloy, that is there should be a cerium matrix that can be etched away leaving only Ag-Ce rods (after directional solidification). The problems encountered with polishing the Ag-76.5at%La sample were similarly experienced with this Ag-Ce composition. Vibratory polishing in water produced severe pitting while a final polishing step performed by hand on a felt wheel with a 0.1 micron diamond and oil suspension produced a more visible microstructure. However, the optical visibility was not of the same quality at that of the Ag-76.5at%La (described later). Repolishing under the same conditions failed to produce better results.
A second composition of silver cerium was investigated with the composition of Ag-81.0at%Ce. With silver being the minority element of this alloys there is potential that, if directional solidification proves to successfully create rods, the cerium matrix can be etched away leaving AgCe rods with air to act as an insulator.

The microstructure at this composition, seen in Figure A-1, varies significantly from the edge of the specimen to the center. Dendrites dominate the region nearest the crucible edge of the sample. The dark colored dendrites reach 200-300 microns toward the interior of the specimen and taper off in the amount of area they occupy until giving way entirely to a lamellar eutectic structure. The dark color of the dendrites suggests oxidized rare-earth. Weight losses for this particular sample were not large enough to be measurable.

Figure A-1. Ag-81.0at%Ce micrographs. (a) 20x near the crucible edge. (b) 50x photo near the center of the button.
Also present are some small, irregularly shaped particles with a high luster. They are present across the sample and don’t seem to have any regularity to their distribution, size, shape or grouping.

All the compositions investigated for this research have some intrinsic aspect that could be useful in a metamaterial along with having some disadvantages unique to each sample. It should be noted that the samples with this composition corroded to powder and broke apart in the weeks following their production. This alone is enough of a negative to eliminate Ag-81.0at%Ce from consideration as a metamaterial.

**Ag-76.5at%La**

Another composition of silver and lanthanum was tried at Ag-76.5at%La. The hope for this composition was to have an alloy with a primarily lanthanum matrix and Ag-La rods. With this composition, the matrix would need to be etched away leaving only conducting rods. There was no evident evaporation of material in the first button created. However, the lanthanum seemed to oxidize fairly significantly during the process of arc melting and flipping, and this seemed to effect the ability to melt the material together and have effective mixing. The sample was flipped and remelted 12 times and yet there was still a clearly visible piece of primary silver in the center of the button that was discovered upon sectioning for metallography. Additional problems occurred during polishing. Lanthanum is attacked by water and is attacked quickly by hot water though the
rate at which the material was degraded came as a surprise and there was a significant amount of pitting present in the sample after one day in a Vibromet polisher with colloidal silica media.

A second button was created with greater care taken to insure the rare earth experienced as little exposure to oxygen as reasonably possible. For most samples, the chamber was evacuated once down then backfilled with argon. For this sample, the chamber was pumped down then backfilled with argon to the working pressure. The chamber was then pumped down again and backfilled with argon to the working pressure. Another level of precaution was taken with the zirconium getter. Instead of melting the getter once before the first melt of the base metals for the alloy, the getter was melted before the silver-lanthanum and then remelted in between every melt-an-flip cycle of the button.

To prevent the pitting from the water attacking the lanthanum in the vibratory polisher, a different final polishing step was taken. The initial polishing steps were the same: hand polishing using successively finer grit sandpaper on a polishing table under running water. A final polishing step was done on a felt wheel with 0.1 micron diamond media in an oil suspension. This step was found to be the best available; polishing in a vibratory polisher with alumina in oil did not produce the quality of surface polish that hand polishing did.
Polishing of this lanthanum dominant silver alloy proved difficult, with the best results coming from hand polishing on a rotating felt wheel with 0.1 micron diamond polishing medial suspended in oil. Optical images are poor at best while SEM images, see Figure A-2, provide a much better view of the microstructure. There are clearly visible elements of both lamella structure along with comparatively large, dark colored dendrite structures. Based on EDS data, the dark areas are primarily lanthanum with silver consisting of less than 2 atomic percent.

![Figure A-2. Ag-76.5at%La micrograph. Sample was polished on a felt wheel with an oil suspension and 0.1 micron diamond media. Striations from polishing can still be](image-url)
Silver Solid Solutions

Two silver solid solutions, Ag-Dy and Ag-Er, were created in order to investigate some properties of these two silver alloys since they both have non-trivial solubility of the rare earth in silver.

Ag-0.9at%Dy

Getting insight into the matrix phase of the Ag-Dy eutectic is important due to the non-insignificant amount of the alloying element that dissolves in the matrix at the eutectic melting temperature of 802˚C. The solubility of dysprosium in silver at the eutectic melting temp is 1.3 atomic percent, and it drops to very near zero as the temperature drops below 500˚C.

A silver based alloy with 0.9 atomic percent dysprosium was arc melted for the purposes of investigating some basic properties of the silver solid solution. EDS data on the solid solution shows a dysprosium content of 0.9 atomic percent which is lower than the literature solubility of 1.3 atomic percent. The small areas of lamella structure seen in Figure A-3 have a dysprosium content comparable to the eutectic of Ag-12at%Dy.
Figure A-3. Ag-0.9at%Dy micrograph.

**Ag-2.0at%Er**

As with the eutectic of silver and dysprosium, the non trivial solubility of erbium in silver is worth investigating further. The matrix solubility of erbium in dysprosium is 3.6 atomic percent at the eutectic melting temperature of 795˚C. A 2 gram button of Ag-2.0at%Er was created in a mini arc melter with negligible loss of mass through being melted and flipped six times for good mixing.

Of all the compositions considered for this research, silver-erbium has the highest solubility of the rare earth in the silver matrix at 3.6 atomic percent. A silver based button with 2.0 atomic percent erbium was created in order to investigate the properties of what the matrix of a directionally solidified silver-erbium eutectic with the composition of 11.5 atomic percent erbium would be.
Under optical magnification, the alloy is primarily clean and metallic colored surface with irregularly shaped and evenly spaced secondary phase with a lamellar pattern inside, (see Figure A-4).

Figure A-4. Ag-2.0at%Er micrograph.

Germanium Line Compounds

Due to particular interest in the germanium-based eutectic alloys, three line compounds were created in order to investigate the properties of the intermetallic phase of the relevant eutectic. Time constraints limited the depth of investigation on these line compounds.

Ge-33.3at%Co

Two line compounds exist on the binary phase diagram for germanium and cobalt. The one of interest for the eutectic has the stoichiometry of Ge$_2$Co and
exists at 33.3 atomic percent cobalt. The goal was a four gram button of the
aforementioned composition. Weight losses were similar to that for Ge-27at%Co
at 3.3 percent. As with the line compounds for Ge-Ti and Ge-Ni, the Ge-Co line
compound button was cut in half with a water cooled, slow-speed diamond saw.
Half was left as cast while the other was annealed at 800 degrees Celsius for 96
hours. Both were then mounted in epoxy, polished through 1200 grit sandpaper
under running water, polished in a Vibromet vibratory polisher for several hours
and spent a final four hours in a vibratory polisher under colloidal silica.

There is a line compound for germanium and cobalt at Ge-33.3at%Co with the
stoichiometry of Ge$_2$Co that is 83.6at% of the two phases present in the eutectic
discussed previously.

The unannealed Ge-Co line compound micrograph, shown in Figure A-5(a),
appears to show long lamella with no particular orientation and small spots of
dark material. Sections of lamella are 50-100 microns long and the spots are
round to oval and are sized on the order of 5-10 microns. After annealing (Figure
A-5(b)) the lamella disappeared while the spots remained and at first inspection
there looked to be cracks running throughout the sample. Upon closer
inspection, the cracks are actually solid material rather than empty space. Even
though mass losses were small (~3wt%), this change would have been enough
to shift the composition from solely Ge$_2$Co to either Ge$_7$Co$_5$ + Ge$_2$Co or Ge$_2$Co + Ge depending on which how the ratio of germanium to cobalt shifted.

![Figure A-5. Ge-33.3at%Co micrographs. (a) This is the as-cast attempt to create a line compound. (b) Is from the same button after annealing for 96 hours at 800°C.](image)

**Ge-50.0a%Ni**

An intermetallic of interest exists at 50 atomic percent germanium and there was an attempt to produce this line compound for further study. Precise measurement of raw metals is important for this and all line compounds and all materials were weighed to 1/100th of a gram (the highest precision available), and weight losses for this button were just under 0.5 percent.

Initially the alloy was sectioned, polished and examined in its as-cast state. Since there is a region of liquid + alpha above 850°C where the GeNi forms, this
alloy needed to be annealed to avoid the presence of Ge$_2$Ni$_3$. The line compound alloy was annealed in an 800°C air furnace for 96 hours. After annealing, the button was mounted in epoxy, polished and inspected optically.

Initially, the as-cast 4 gram button of Ge-50at%Ni was cut in half, mounted and polished and viewed under an optical microscope. The water cooled copper crucible of the arc melter in which this alloy was created produces a non-equilibrium cooling condition that is apparent when viewing the micrograph. The majority of the area seen is taken by cored sections with interspersed areas of tightly wound lamellar structure, see Figure A-6.

![Figure A-6. Ge-50at%Ni micrographs. (a) As-cast line compound and (b) line compound after 96 hours annealing.](image)

After annealing the other half of the button, the microstructure changed markedly from the as-cast condition. The bulk of the micrograph consists of large areas of
lightly colored material that is smooth and uniform save for some small amount of pitting. Between these uniform areas are dark bands of material approximately 1-3 microns across. The appearance of these bands is similar to that of grain boundaries in that they link together and run like a web across the sample.

EDS data of only the uniform areas gives atomic percentages of nickel and germanium of approximately 49 and 48 percent respectively. The remaining 3 percent registers as copper.

**Ge-33.3at%Ti**

At 33.3 atomic percent titanium there exists the line compound that is the intermetallic phase the titanium-germanium eutectic, Ge₂Ti. A button with the composition Ge-33.3at%Ti was created. The specimen was cut in half; one half was polished in the as-cast state while the other was annealed before being polished. The piece was annealed at 800°C in an air furnace for 96 hours and was then mounted and polished.

The intermetallic of Ge-9.2at%Ti has the formula Ge₂Ti and it was this line compound that was aimed for in this last alloy. As shown in Figure A-7, the as-cast line compound shows what appears to be coring in some parts of the micrograph.
As with the other germanium-based line compounds created for this work, Ge-33.3at%Ti is a peritectic and as such needs to be annealed to reduce or eliminate the presence of the primary phase Ge$_5$Ti$_6$. After annealing, mounting and polishing the sample, optical micrographs were taken and show at least two phases. As with the other germanium-based alloys, copper was shown to be present at approximately 2.5 atomic percent. Not seen before was the presence of aluminum which is present in amounts ranging from 0.3 to 2.3 atomic percent depending on where on the surface EDS data was taken. The source of this aluminum is unknown and did not appear in other EDS data. Side-by-side micrographs of annealed and unannealed Ge-Ti line compound are seen below in Figure A-7.

![Figure A-7. Ge-33.3at%Ti micrographs. (a) As-cast line compound and (b) after annealing for 96 hours.](image-url)
VITA

Ethan Elder Fox was raised just south of the University of Tennessee and has been a Vol fan since birth. After acquiring a Bachelor of Science in mechanical engineering from Tennessee Tech University he began work as a Post-BS student at Oak Ridge National Lab. It was at ORNL he acquired experience in research and was convinced by his mentor to attend graduate school.