SYNTHETIC APPROACHES TO METAL CHALCOGENIDE NANOSTRUCTURES

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ABSTRACT

Both transition metal chalcogenides and rare earth metal chalcogenides are of interest for their electronic, optical, and/or magnetic properties, which have been largely demonstrated in the bulk. Synthesizing metal chalcogenide materials on the nanoscale is advantageous for their use in application since properties can be enhanced or fine-tuned according to size and shape. In particular, we are interested in synthesizing nanostructures of the superconducting iron selenide material, as well as the divalent samarium chalcogenides. However, these materials can exhibit several different phases, including $\text{MX}_2$, $\text{M}_3\text{X}_4$, $\text{M}_2\text{X}_3$ and $\text{MX}$ (where $\text{M} = \text{Fe} \text{ or Sm}$ and $\text{X} = \text{S}$ or $\text{Se}$). Additionally, the FeSe phase exhibits two structure types of which the tetragonal phase is superconducting and the hexagonal phase is nonsuperconducting. The synthetic conditions favoring each phase or structure type is not well known or understood. Given the similar phases exhibited by both iron selenide and the samarium chalcogenides, similar considerations for synthetic approaches can be applied in both systems. Additional challenges to be addressed in these systems lies in establishing morphology and composition control.

By investigating various precursors and reaction conditions for particle growth via the hot injection method, we have demonstrated that the precursor ratio largely influences the iron selenide phase, whereas reaction time dictates the structure type for the thermodynamically favored tet-FeSe. Although, superconductivity in iron selenide is extremely sensitive to composition, this work also demonstrates morphology control for cubic nanoplatelets of tet-FeSe revealing its naturally
layered structure. By investigating alkali and alkaline metal intercalation of tet-FeSe, we may be able to further establish composition control for superconductivity.

Various precursors have also been investigated for the synthesis of samarium chalcogenide materials via solid state and solution-phase approaches. Due to samarium’s oxophillic nature, the Sm$_3$X$_4$ phase is favored. As a result of the relative stability of trivalent samarium, we demonstrate the synthesis of Eu$_{1-x}$Sm$_x$Se nanomaterials, in which samarium may act as an effective electron donor, thereby enhancing the semiconducting properties of EuSe. At low doping levels, where $x=0.10$, a shift in the diffraction peaks is observed, indicating the incorporation of Sm$^{3+}$ within the europium selenide lattice.

Herein, we discuss the similarities and differences between the synthetic conditions favoring phase, morphology, and composition for iron selenide and samarium chalcogenide materials.
The research and writing of this thesis is dedicated to my loving mother, Emily Ingram, who has continuously supported me in my endeavors and encouraged me to never give up on my dreams.
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<tr>
<td>Bis(trimethylsilyl)sulfide</td>
<td>(TMS)$_2$S</td>
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<td>Borane $t$-butyl Amine Complex</td>
<td>TBAB</td>
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<td>Cetyltrimethylammonium Bromide</td>
<td>CTAB</td>
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<td>Diethylammonium Diphenyldiselenophosphinate</td>
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<td>Oleic Acid</td>
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<td>Oleylamine</td>
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<td>Potassium Diphenyldiselenophosphinate</td>
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<td>Powder X-ray Diffraction</td>
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<td>Scanning Electron Microscopy</td>
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<td>Tetragonal Iron Selenide</td>
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<tr>
<td>Tetrahydrofuran</td>
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<td>Transmission Electron Microscopy</td>
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CHAPTER 1. INTRODUCTION

Interest in metal chalcogenides has grown as a result of the optical, electronic, and/or magnetic properties exhibited. Establishing control over these properties can enable the development of new functional materials for today’s advancing technology. The metal chalcogenide materials we are interested in are classified as $M_xX_y$, where $M = \text{a divalent transition metal or lanthanide metal}$ and $X = \text{S}^{2-}, \text{Se}^{2-}, \text{or Te}^{2-}$. The properties of transition metal chalcogenides and rare earth metal chalcogenides are uniquely different based on the hybridization of the $d$ and $f$ orbitals, respectively.\(^1\) However, the evolution of the band diagrams for both classes of materials is quite similar (Figure 1.1).

![Figure 1.1. Schematic representation for the evolution of energy level structure. Reproduced with permission from John Wiley and Sons.\(^2\)](image)

In considering the simplest molecule, $H_2$, two atomic orbitals give rise to two molecular orbitals – one bonding and one antibonding molecular orbital. This model expands as the number of atoms increases, resulting in an increase of molecular orbitals. Semiconductor nanocrystals can be considered a cluster containing a few tens to a few thousand atoms, giving rise to discreet energy bands – a valence band (VB) and a conduction band (CB). The energy difference between these bands is the band gap ($E_g$) which is unique for each semiconductor. Extending to the bulk results...
in a decrease in the band gap and potentially an overlap between the valence and conduction bands.\textsuperscript{2} Therefore, this model indicates the importance of establishing size control for the synthesis of nanomaterials in which unique semiconducting properties can be exploited.

The widely-studied II-VI semiconductors, such as CdSe, are classic systems exemplifying important structure-function relationships on the nanoscale for semiconductors. The synthesis of these colloidal nanocrystals allows for full exploitation of size effects for the engineering of material properties (Figure 1.2). In fact, the band gap can be tuned by changing the nanomaterial size, resulting in differing optical properties. Because of the range of colors exhibited in CdSe colloidal nanocrystals, they are being employed in quantum dot televisions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{cdse_nanocrystal.png}
\caption{Schematic representation of CdSe nanocrystal size on the energy level structure. Reproduced from Ref. 3 with permission from The Royal Society of Chemistry.\textsuperscript{3}}
\end{figure}

Several semiconducting metal chalcogenides also exhibit interesting magnetic properties including ferromagnetism and antiferromagnetism. Figure 1.3 shows representations of paramagnetism, ferromagnetism, and antiferromagnetism, where the arrows represent the magnetic moment caused by unpaired electrons on individual atoms. Paramagnetic materials lack internal ordering and results in no net magnetic moment. In a ferromagnet, the magnetic moments
align, resulting in an overall magnetic moment in one direction. Antiferromagnetism is highly ordered, but the moments are aligned antiparallel and, as a result, cancel out. Both ferromagnetism and antiferromagnetism are defined by their magnetic ordering temperatures, given by the Curie temperature, $T_c$, and Neel temperature, $T_N$, respectively. Ferrimagnetism is similar to antiferromagnetism in that magnetic moments are aligned antiparallel; however, there exists a stronger moment in one direction resulting in an overall magnetic moment in one direction, similar to ferromagnetism. At temperatures above the magnetic ordering temperatures, the materials become paramagnets.

![Diagram of paramagnetism, ferromagnetism, and antiferromagnetism](image.png)

**Figure 1.3. Schematic representation of paramagnetism, ferromagnetism, and antiferromagnetism.**

Another electronic property of interest is superconductivity in which a material exhibits zero resistance below a specific temperature, $T_c$, implying that a current could flow indefinitely within the material. For instance, Figure 1.4 show the resistivity versus temperature of $\text{YBa}_2\text{Cu}_3\text{O}_7$, in which the $T_c$ is marked and the resistance drops to zero. This phenomenon arises due to the formation of Cooper pairs, or the loose association of electrons into pairs that move cooperatively through the crystal lattice. As one electron travels through the lattice, it creates a charged pathway for another electron to travel. Because of this pairing of electrons, superconductors act as perfect diamagnets and can also expel a magnetic field by the Meissner effect. Superconductors are of
interest for application in magnetic resonance imaging (MRI), the transport of electricity, and magnetic levitation trains. However, most superconductors have transition temperatures ($T_c$) too low for many applications, and there is strong interest in discovering new high temperature superconductors as well as increasing the corresponding superconducting transition temperatures. Studying these materials on the nanoscale may provide further insight into the superconducting mechanism.

![Figure 1.4. Resistivity of the YBa$_2$Cu$_3$O$_7$ superconductor. Reproduced with permission from Springer.](image)

Because properties can be enhanced on the nanoscale as well as the increasing demand for small scale materials for devices, several routes have been reported for the synthesis of nanomaterials.$^{5-8}$ Overall, three main challenges for the synthesis of nanomaterials exist and continue to be studied. These include establishing (1) phase control for $M_xX_y$, (2) shape control, and (3) composition control via doping. These challenges will be addressed in this thesis for the synthesis of iron chalcogenides and samarium chalcogenides, in which similarities and differences
can be observed. Of the possible synthetic routes for nanomaterials, the most widely is the hot injection method, whereas the solvothermal approach is widely used for shape control and the synthesis of single crystals. The solvothermal approach involves a Teflon-lined autoclave loaded with precursors and a solvent which is then sealed and heated in a furnace at temperatures greater than the boiling point of the solvent. In turn, this leads to the supersaturation of the solvent by a product which generally produces highly crystalline material upon slow cooling. Common solvents in this approach include ethylenediamine (bp=188°C) and deionized water (bp=100°C). However, the kinetics and specific reaction conditions to establish size, shape, and/or composition control is not well studied or understood.\textsuperscript{5,7}

Alternatively, the hot injection method is a widely used approach that has been studied for several metal chalcogenide systems. Here, the arrested precipitation of homogeneous nanoparticles can be observed from the injection of precursors in a high boiling point capping ligand.\textsuperscript{5} A variety of precursors have been investigated for the synthesis of metal chalcogenide nanomaterials with phase control, including elemental precursors for both metal and chalcogen, metal complexes or salts with a corresponding chalcogen containing compound or salt, and single source precursors featuring M-X bonds. A wide range of precursors continue to be investigated, and selecting appropriate precursors continues to be a challenge since metal chalcogenide phase cannot be directly predicted from the precursor source. However, we anticipate that choosing precursors with the appropriate oxidation state of interest and in an appropriate stoichiometric ratio may aid in targeting a specific phase as well as avoid troublesome redox chemistry. In the hot injection method, the selected precursors are thermally decomposed in the presence of coordinating solvents which perform several essential roles for the synthesis of nanomaterials. In addition to providing
a solvent stable at the high temperatures necessary for the thermal decomposition of precursors, the solvent also acts as a capping ligand which forms a protective coating on the nanomaterial surface and strongly influences the nucleation and growth kinetics of nanomaterials. This is important for controlling size and shape. Ideal coordinating solvents contain a polar head group with donor atoms that can interact with metal ions in solution via a Lewis acid-base interaction. The solvent should also have a non-polar hydrocarbon tail which may provide steric effects to influence size or shape. Common capping ligands include alkyl amines, like oleylamine (bp=350°C) and hexadecylamine (bp=330°C), as well as fatty acids, like oleic acid (bp=195°C) (Figure 1.5). Octadecene (bp=315°C) may also be employed as a non-coordinating solvent in combination with a capping ligand to dilute the capping ligand concentration in solution as well as to help maintain a high temperature.³

Figure 1.5. **Commonly used capping ligands or solvents.** Oleylamine (top left), hexadecylamine (top right), oleic acid (bottom left), and octadecene (bottom right).

The formation of nanocrystals via the hot injection method occurs in a series of well-studied steps, known as La Mer’s Mechanism⁹ (Figure 1.6). Upon injection, the precursors decompose into monomers to quickly form a critical concentration of stable nuclei. Finally, with time, the nuclei grow into larger nanocrystals. Once the desired size and/or shaped has been achieved, the growth phase can be terminated upon cooling the reaction mixture.³ A related approach to the hot injection method is the ‘heat-up’ method, in which the precursors and capping ligand are heated to the desired temperature simultaneously.¹⁰ However, this route tends to lead to
the formation of larger polydispersed nanoparticles because of the lack of control over nucleation.\textsuperscript{11}

In addition to interest in size control for the synthesis of metal chalcogenide nanostructures, the shape or morphology can greatly enhance properties of interest for application. For instance, anisotropic growth of nanowires or nanorods are advantageous in providing a direct pathway for electrons to travel, when compared to other nanomaterial shapes like spheres or cubes. Synthetically, solvothermal routes have been explored for anisotropic growth. In the hot injection method, appropriate capping ligands can provide morphology control.\textsuperscript{3,13} The polar head group of a capping ligand coordinates to an hkl face of a crystal and can act to influence growth in a certain direction (Figure 1.7). Also, the length of the alkyl chain in coordinating solvents can introduce steric effects for shape control.\textsuperscript{14} In fact, shorter chain ligands can result in branching of the material, resulting in the growth of tetrapods.\textsuperscript{14,15} Combinations of capping ligands in a co-solvent system can also be employed to influence morphology.\textsuperscript{16} Furthermore, in considering possible growth mechanisms, it is also important to consider the crystal structure, which may naturally

\textbf{Figure 1.6. Nucleation and growth mechanism of metal chalcogenide nanocrystals via the hot injection method.} Reprinted with permission from Garcia-Rodriguez, R. \textit{et.al. Chem. Mater.} 2013, 25, 1233. Copyright 2013 American Chemical Society.\textsuperscript{12}
adopt certain shapes. For instance, compounds of the tetragonal structure type contain an elongated $c$-axis and can grow more quickly along this axis forming a rod. Thus, establishing control for growth along the $c$-axis may result in the formation of nanowires.

![Figure 1.7. Schematic representation of morphology control with capping ligands.](image)

(A) nanoparticle capped with shorter chain ligands and (B) role of longer chain capping ligands for nanowire formation.

Given the synthetic considerations for shape and size control, establishing phase control is also of importance. The iron and samarium chalcogenides exhibit several stable phases and/or structure types, including $\text{MX}$, $\text{MX}_2$, $\text{M}_2\text{X}_3$, and $\text{M}_3\text{X}_4$. Divalent metal can be seen in $\text{MX}$, trivalent metal is observed in $\text{M}_2\text{X}_3$, and $\text{M}_3\text{X}_4$ exhibits mixed valency (divalent and trivalent). The literature argues the valency in $\text{MX}_2$ in which some reports support divalent metal with a dichalcogenide, such as disulfide ($\text{S}_2^{2-}$), and other reports indicate the metal is tetravalent. Iron exhibits several stable oxidation states, whereas samarium is typically trivalent and occasionally divalent. Overall, the factors favoring metal oxidation state for each phase are generally unknown and may differ from the transition metals to the lanthanide metals. Since a high level of phase purity is necessary for application, this indicates the need to establish precise control in metal chalcogenide nanomaterials. Synthetically, phase control can be targeted via the appropriate precursor; however, there still exist several other conditions and factors that can influence phase.
Composition control in nanomaterials via doping is also of interest and can also influence properties. Doping is the intentional introduction of impurity atoms or molecules into the host lattice. Since the iron chalcogenides exhibit a layered structure (Figure 1.8), doping can be achieved via chemical intercalation, or the fitting of other atoms, ions, or molecules into the space between layers. The interaction between these layers is via van der Waals forces or weak chemical bonding. Intercalation can increase the interlayer distance and serve as a charge carrier between one conducting metal chalcogenide layer to another, thereby affecting the chemical and physical properties of corresponding compounds. We are interested in intercalation because it has been shown to enhance the superconducting transition temperature in FeSe, which will be discussed in more detail in Chapter 3.

In the rare earth chalcogenides, doping can be accomplished via site substitution. Here, an atom or ion of similar size and charge replaces the site of the host atom or ion. Of the rare earths, europium chalcogenides have been the most widely studied because of their highly coupled magnetic and electronic properties. Such properties can be enhanced by increasing the concentration of electrons in the conduction band. Doping with a non-redox active metal, such as trivalent gadolinium, provides a delocalized electron to give $\text{Eu}^{2+} \cdot x\{\text{Gd}^{3+}(e^-)\}_x X$, where $X = \text{O, S, Se, or Te}$, which is promoted to the conduction band. Of the lanthanide metals, Gd$^{3+}$ is especially stable because of its half-filled $f$-orbital making it an ideal electron donor for these systems; however, other lanthanide metals may also similarly act as electron donors.
In this thesis, I will address the synthetic approaches and considerations for establishing phase, morphology, and composition control for both transition metal chalcogenides and rare earth metal chalcogenides on the nanoscale. Our interest in first row transition metals and first row lanthanide metals stems from their ability to exhibit magnetism; however, their chemistry is uniquely different. Similar synthetic approaches have been taken to target nanomaterials for each system, and the similarities and differences will be presented in detail. In Chapters 2 and 4, I will describe approaches for phase control in iron selenide and samarium chalcogenide nanomaterials. Morphology control for iron selenide nanostructures will also be discussed. Chapters 3 and 5 will focus on composition control via the chemical doping of these systems in an effort to fine-tune the
resulting electronic and/or magnetic properties of interest. Lastly, Chapter 6 will describe additional work performed in developing the General Chemistry Laboratory for Majors course format at Georgetown University. Although unrelated to the bulk of this thesis, it is of importance to understand the basis in which instructors can prepare students for a successful career in science through inquiry-based learning.
CHAPTER 2. SYNTHETIC APPROACHES TO IRON SELENIDE NANOMATERIALS WITH PHASE AND MORPHOLOGY CONTROL

2.1 Introduction

Early transition metals are earth abundant and inexpensive, and materials containing transition metals have seen extensive research for numerous applications. Of them, iron chalcogenide compounds have attracted much interest for their electronic and/or magnetic properties with potential applications including photovoltaics, supercapacitors, and memory storage devices. However, these systems are quite complex, each having multiple possible stable phases and/or structure types. Their use in applications generally requires a high level of phase purity, and it is therefore important to understand the conditions for phase control.

For example, the iron sulfide system exhibits seven different phases shown in Figure 2.1, and much work has been done to establish phase control in this system. Of the possible phases, the cubic FeS$_2$ phase, known as pyrite, has received considerable attention for application in photovoltaic devices. Synthetically, the divalent iron precursor, FeCl$_2$, is observed to favor pyrite via the hot injection method but Alivisatos reports an iron (III) single source precursor that decomposes to form pyrite via solvothermal approaches. The iron sulfide system continues to be heavily studied which has resulted in the very recent discovery of superconductivity in tetragonal FeS with a superconducting transition temperature of 5K.
Alternatively, iron selenide has also attracted attention recently as a result of the discovery of superconductivity in the tetragonal phase of bulk FeSe (tet-FeSe) with a superconducting transition temperature of 8.5K.26 The work described herein was motivated by this discovery as well as the following efforts in enhancing the critical temperature of iron selenide with pressure,27 intercalation chemistry, or alternative routes28–30 that have been reported in the literature. Since 2008, much work has been dedicated to understanding the factors affecting superconductivity in iron selenide.31,32 However, the synthesis of the tet-FeSe is quite challenging, given the possible phases of iron selenide. In addition to tet-FeSe (Figure 2.2A), there also exists the NiAs-structure
type (hex-FeSe, Figure 2.2B), Fe$_5$Se$_4$ (monoclinic), Fe$_7$Se$_8$ (hexagonal) and FeSe$_2$ (cubic and orthorhombic).

**Figure 2.2. Crystal structures of iron selenide.** (A) tet-FeSe and (B) hex-FeSe. Fe and Se atoms are shown in red and yellow, respectively. Reproduced with permission from IOP Publishing.  

Although tet-FeSe has received considerable attention in recent years, the other iron selenide phases also exhibit unique electronic and/or magnetic properties. For example, FeSe$_2$ has a direct band gap of 1.0 eV making it a promising candidate for solar cells. The solvothermal synthesis of FeSe$_2$ mirrors that of FeS$_2$ in which the pyrite system is generally well-known and studied. Both Fe$_7$Se$_8$ and Fe$_3$Se$_4$ are ferrimagnetic with Curie temperatures of 450K and 314K, respectively. Synthesizing Fe$_3$Se$_4$ on the nanoscale via a ‘heat-up’ approach has resulted in giant coercivity which is of interest for permanent magnets and data storage devices.

Such desirable properties showcase the need to establish a synthetic route in which to control phase with small adjustments to the synthetic conditions. This has been demonstrated via a solvothermal approach, in which varying amounts of sodium hydroxide are reported to influence the iron selenide phase formed for FeSe$_2$, tet-FeSe, and Fe$_3$Se$_4$. The resulting nanosheets of tet-FeSe are superconducting with tunable critical temperatures from 3.2-10K, depending on the
reaction time employed. Another report suggests a strategy for targeting the FeSe phase via selenium extraction from selenium-rich phases, like Fe$_3$Se$_4$, but the resulting tet-FeSe materials do not exhibit superconductivity.$^{38}$ Overall, efforts to establish phase control in iron selenide nanomaterials via the hot injection method have not been established or reported.

In addition to phase control, methods for establishing composition control are especially important for the tet-FeSe system because of the extreme sensitivity of superconductivity to the stoichiometry between iron and selenium.$^{31}$ In the bulk synthesis of tet-FeSe, it has been found that compositions of Fe$_{1.01}$Se and Fe$_{1.02}$Se are superconducting ($T_c = 8.5$K and 5K, respectively), whereas the Fe$_{1.03}$Se composition is nonsuperconducting (Figure 2.3). These subtle differences in stoichiometry and the resulting effects on properties, pose an added challenge in the synthesis of superconducting FeSe, which has not been reported on the nanoscale.

![Figure 2.3. Low field susceptibility of Fe$_x$Se.](image)

**Figure 2.3. Low field susceptibility of Fe$_x$Se.** Superconductivity is observed in Fe$_{1.01}$Se and Fe$_{1.02}$Se, whereas Fe$_{1.03}$Se is nonsuperconducting. Reproduced with permission from the American Physical Society.$^{31}$
There exist several possible routes for the synthesis of iron chalcogenide nanomaterials, in which the most widely reported methods are that of the hot injection method and solvothermal synthesis. In both routes, various precursors have been utilized, including elemental iron or Fe(CO)$_5$, elemental sulfur or selenium, single source precursors (SSPs), and Fe(II) or Fe(III) salts. In his recent review of synthetic routes for iron chalcogenide materials, O’Brien argues that nanoparticle phase can be achieved by the proper choice of iron source. However, in this work, we have found that one iron source and one selenium source exclusively can yield any of the iron selenide phases, in which the reaction conditions are important for the iron selenide phase and/or composition formed.

Furthermore, morphology, or shape control, is also of interest. Specifically, since tet-FeSe is a naturally layered material, it would be advantageous to study morphology control for one-dimensional (1D) and two-dimensional (2D) growth. In terms of 1D growth, growth along the c-axis of tet-FeSe could afford the opportunity to synthesize iron selenide nanorods or nanowires. To date, only one example of superconducting iron selenide nanowires has been reported. However, the morphology more closely resembles a cable with several impurities (carbon, Pd, Au) and the superconducting fraction of the synthesized material is quite low, indicating that only a small portion of the material is superconducting (Figure 2.4). These impurities largely result from the synthetic approach in utilizing chemical vapor deposition. In this approach, precursors are heated to 800°C, vaporized in a carrier gas, such as nitrogen, and deposited on a metal catalyst, which then aids in 1D growth. In this case, the catalyst becomes integrated into the material, resulting in palladium and gold dopants in the FeSe material.
Herein, we describe the synthesis of iron selenide nanomaterials with phase control for tet-FeSe, hex-FeSe, Fe₃Se₄, and FeSe₂. Unlike previous reports, we can influence the phase as well as the morphology of the iron selenide materials formed with small and controlled changes to the synthetic conditions via the hot injection method. We will also discuss approaches to establish composition control for the superconducting Fe₁.₀₁Se. These results may provide insight into the factors that affect their resulting magnetic or superconducting properties.

2.2 Experimental Section

2.2.1 General Information

Cetyltrimethylammonium bromide (CTAB), diethylamine, diphenylphosphine, hexadecylamine (HDA, 90%), hydrazine, iodine, iron (II) acetate, iron (II) chloride tetrahydrate, oleic acid (OA), oleylamine (OLA, 70%), selenium powder, selenous acid, and toluene were

Figure 2.4. FeSe nanocable characterization. Magnetic susceptibility and TEM of FeSe nanocable ensemble. Reprinted with permission from Mishra, S. et.al. ACS Nano. 2013, 7, 1145. Copyright 2013 American Chemical Society.
purchased from Sigma-Aldrich. Diethyl ether, ethanol, hexanes, and isopropanol were obtained from Fisher Scientific. All chemicals were used as received. Diethylammonium diphenyldiselenophosphinate (DSP) was synthesized as previously reported. In brief, diphenylphosphine and selenium powder were mixed in dry ethanol under N\textsubscript{2} atmosphere. Diethylamine was added via syringe and the reaction was heated to 60\textdegree C for approximately 1 hour until the selenium powder had reacted completely. The product precipitated upon cooling and was collected via vacuum filtration and washed with cold diethyl ether.

X-ray powder diffraction (PXRD) patterns were obtained using a Rigaku Ultima IV X-Ray powder diffractometer with Cu K\textsubscript{\alpha} radiation and a DTex detector. SEM images were taken with a Zeiss SUPRA 55-VP Scanning Electron Microscope at an acceleration voltage of 9-20 kV with an in-lens detector. High resolution TEM was performed with a JEOL JEM 2100F Field Emission Gun Transmission Electron Microscope at 200 kV at the University of Maryland Nanoscale Imaging Spectroscopy and Imaging Laboratory. Low field magnetic susceptibility measurements were obtained from 5-20K on a Quantum Design MPMS 3 SQUID Magnetometer at the University of South Carolina.

2.2.2 Phase and Structure Type Control of Iron Selenide

Fe\textsubscript{3}Se\textsubscript{4} via hot injection method. A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. OLA (10.0 mL) was added to the round bottom flask and degassed at 120\textdegree C for 1 hour. The apparatus was purged with nitrogen, and the OLA refluxed at 330\textdegree C. Meanwhile, the precursor solution was prepared in the glove box by dissolving iron acetate (0.0350 g, 0.2012 mmol) and DSP (0.1672 g, 0.4007 mmol) in OLA (5.0 mL), forming a brown solution. The precursor solution was injected into the hot OLA, resulting in a black color.
The reaction mixture heated 5-180 minutes and then slowly cooled to room temperature. The resulting black powder was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD analysis of a representative sample, SEI-168-A, showed pure phase Fe$_3$Se$_4$ (PDF#01-071-2251): 18.274°, 4.8509 Å; 32.862°, 2.7232 Å; 33.360°, 2.6837 Å; 33.820°, 2.6483 Å; 43.560°, 2.0760 Å; 44.379°, 2.0396 Å; 51.621°, 1.7692 Å; 52.142°, 1.7527 Å; 63.442°, 1.4650 Å; 70.702°, 1.3313 Å.

**hex-FeSe via hot injection method.** A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. OLA (10.0 mL) was added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and the OLA refluxed at 330°C. Meanwhile, the precursor solution was prepared in the glove box by dissolving iron acetate (0.0692 g, 0.3979 mmol) and DSP (0.0836 g, 0.2004 mmol) in OLA (5.0 mL), forming a brown solution. The precursor solution was injected into the hot OLA solution, resulting in a black color. The reaction mixture heated 5 minutes and then slowly cooled to room temperature. The resulting black powder was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD analysis of SEI-77-A showed pure phase hex-FeSe (PDF#01-071-4479): 32.480°, 2.7544 Å; 42.240°, 2.1378 Å; 50.440°, 1.8078 Å; 55.342°, 1.6587 Å; 61.219°, 1.5128 Å; 67.760°, 1.3818 Å.

**tet-FeSe via hot injection method.** A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. OLA (10.0 mL) was added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and the OLA refluxed at 330°C. Meanwhile, the precursor solution was prepared in the glove box by dissolving iron acetate (0.0696 g, 0.4002 mmol) and DSP (0.0836 g, 0.2004 mmol) in OLA (5.0 mL), forming
a brown solution. The precursor solution was injected into the hot OLA solution, resulting in a black color. The reaction mixture heated 20-60 minutes and then slowly cooled to room temperature. The resulting mixture was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD analysis of a representative sample, SEI-89-A, showed pure phase tet-FeSe (PDF#01-085-0735): 16.058°, 5.5150Å; 28.520°, 3.1272Å; 37.258°, 2.4114Å; 47.202°, 1.9240Å; 47.980°, 1.8946Å; 55.536°, 1.6534Å; 56.800°, 1.6195Å; 70.259°, 1.3386Å. **FeSe$_2$ via hot injection method.** A three-neck round bottom flask was equipped with a condenser, thermocouple adapter, and stopper. OLA (5.0 mL) and OA (4.3741 g, 0.0155 mol) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and the OLA:OA mixture was allowed to reflux at 330°C. Meanwhile, the precursors were prepared outside the glove box by dissolving iron acetate (0.0349 g, 0.2007 mmol) and DSP (0.1659 g, 0.3976 mmol) in OLA (5.0 mL), forming a brown solution. The precursor solution was injected into the hot capping ligand solution, resulting in a black color. The reaction mixture heated 60 minutes and then slowly cooled to room temperature. The resulting black powder was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD analysis of SEI-61-A showed pure phase orthorhombic FeSe$_2$ (PDF#01-074-0247): 18.299°, 4.8442Å; 31.359°, 2.5802Å; 35.019°, 2.5603Å; 36.400°, 2.4662Å; 48.339°, 1.8813Å; 51.059°, 1.7873Å; 54.002°, 1.6967Å; 64.181°, 1.4500Å. **FeSe$_2$ via solvothermal methods.** Iron (II) chloride (0.0255 g, 0.2012 mmol), DSP (0.2506 g, 0.6006 mmol), CTAB (0.0731 g, 0.2006 mmol) and distilled water (10 mL) were added to a Teflon-lined stainless steel autoclave (25 mL capacity). The autoclave was heated and maintained at 260°C for 8 hours and then gradually cooled to room temperature. The resulting
black product was collected via centrifugation and washed with toluene and isopropanol several times. PXRD analysis of a representative sample, SEI-92-A, showed pure phase orthorhombic FeSe_2 (PDF#01-079-1892): 29.298°, 3.0459Å; 31.078°, 2.8753Å; 34.800°, 2.5759Å; 36.181°, 2.4807Å; 48.162°, 1.8878Å; 50.882°, 1.7931Å; 53.902°, 1.6996Å; 57.540°, 1.6005Å; 64.060°, 1.4524Å; 76.882°, 1.2390Å.

2.2.3 Morphology Control of Iron Selenide

Se Nanowires. The synthesis of Se nanowires was adapted from the literature. In a three-neck round-bottom flask, hydrazine (4.55 mL) was added to distilled water (125 mL), which was then heated to 100°C and allowed to equilibrate. Meanwhile, selenous acid solution was prepared by dissolving selenous acid (0.1279 g) in distilled water (25 mL). The selenous acid solution was added to the reaction flask via syringe resulting in a brick-red color. The reaction mixture refluxed at 100°C for 10 minutes and then cooled slowly for 20 minutes. The solution was transferred to a bottle and stored in a dark cabinet for 10 days. The resulting black product was isolated via centrifugation and washed with distilled water several times. PXRD analysis of SEI-30-A showed pure phase Se (PDF#00-006-0362): 23.620°, 3.7637Å; 29.800°, 2.9957Å; 41.440°, 2.1772Å; 43.720°, 2.0688Å; 45.460°, 1.9936Å; 51.820°, 1.7629Å; 56.199°, 1.6354Å; 61.741°, 1.5013Å; 65.321°, 1.4274Å. SEM images revealed wire and rod morphologies.

tet-FeSe cubic plates via hot injection method. A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. OLA (5.0 mL) and HDA (3.9108 g, 0.0162 mol) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and the capping ligand mixture refluxed at 330°C. Meanwhile, the precursor solution was prepared in the glove box by dissolving iron acetate (0.0698 g, 0.4013
mmol) and DSP (0.0828 g, 0.1984 mmol) in OLA (5.0 mL), forming a brown solution. The precursor solution was injected into the hot capping ligand solution, resulting in a black color. The reaction mixture heated 20 minutes and then slowly cooled to room temperature. The resulting black product was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD of SEI-91-A was obtained to show tet-FeSe (PDF#01-085-0735): 15.996°, 5.5361Å; 28.599°, 3.1187Å; 37.339°, 2.4063Å; 47.382°, 1.9171Å; 48.042°, 1.8923Å; 55.604°, 1.6515Å; 56.918°, 1.6165Å; 70.340°, 1.3373Å.

**Fe₃Se₄ diamond plates via hot injection method.** A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. OLA (10.0 mL) was added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and the capping ligand mixture refluxed at 330°C. Meanwhile, the precursor solution was prepared in the glove box by dissolving iron acetate (0.0695 g, 0.3996 mmol) and DSP (0.1668 g, 0.3595 mmol) in OLA (5.0 mL), forming a brown solution. The precursor solution was injected into the hot capping ligand solution, resulting in a black color. The reaction mixture heated at least 30 minutes and then slowly cooled to room temperature. The resulting black product was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD of SEI-157-A was obtained to show Fe₃Se₄ (PDF#03-065-5820): 33.078°, 2.7059Å; 33.519°, 2.6713Å; 43.320°, 2.0870Å; 44.139°, 2.0501Å; 51.378°, 1.7770Å; 51.861°, 1.7616Å; 63.183°, 1.4704Å; 70.557°, 1.3337Å. SEM and TEM images revealed diamond plates.

**2.2.4 Composition Control of tet-FeSe**

**Deintercalation of interstitial iron via solid state routes, SEI-109-A.** A prepared sample of tet-FeSe (30.2 mg, 0.2240 mmol) and iodine (7.9 mg, 0.3113 mmol) were loaded into a glass
tube which was evacuated and sealed. The tube was then heated in the furnace at 200°C for 18 hours. Once cooled, the product was washed with methanol and centrifuged to remove iron (II) diiodide. PXRD analysis of the black powder showed Se (PDF#01-086-2246), FeSe₂ (PDF#01-082-0269), and tet-FeSe (PDF#01-073-6939): 23.453°, 3.7901Å; 29.646°, 3.0109Å; 34.809°, 2.5752Å; 35.597°, 2.5200Å; 43.598°, 2.0743Å; 45.355°, 1.9979Å; 51.681°, 1.7673Å; 53.998°, 1.6968Å; 56.047°, 1.6395Å; 62.444°, 1.4860Å.

**Deintercalation of interstitial iron via solution phase routes.** A 0.01 M iodine solution was prepared by dissolving iodine (50.3 mg) in hexanes (20 mL), resulting in a purple color. Three samples were prepared by adding stoichiometric amounts of a prepared sample of tet-FeSe in hexanes to iodine solution with a total volume of 10 mL, targeting FeSe₂, Fe₃Se₄, and Fe₇Se₈, respectively. The sample vials stirred at room temperature for 2 hours and then centrifuged and washed with hexanes and ethanol, resulting in black powders. PXRD analysis of SEI-245-A showed Se (PDF#01-086-2246) and tet-FeSe (PDF#01-085-0735): 23.381°, 3.8016Å; 28.538°, 3.1252Å; 29.540°, 3.0215Å; 43.542°, 2.0768Å; 47.222°, 1.9232Å; 51.359°, 1.7776Å; 55.657°, 1.6501Å. PXRD analysis of SEI-245-B and SEI-245-C showed similar diffraction patterns with lower crystallinity.

### 2.3 Results and Discussion

#### 2.3.1 Phase and Structure Type Control of Iron Selenide

The synthesis of iron selenide via the hot injection method has afforded the ability to elucidate several iron selenide phases and structure types, including tet-FeSe, hex-FeSe, FeSe₂, and Fe₃Se₄, with small, yet controlled, changes to the synthetic conditions. The conditions studied for iron selenide phase include precursor preparation, precursor ratio, capping ligand selection,
and reaction time, which are summarized in Table 2.1. Of the reaction conditions investigated, reaction time was found to be the largest contributing factor in synthesizing phase pure tet-FeSe.

Table 2.1. Reaction conditions for iron selenide phase control via the hot injection method.

<table>
<thead>
<tr>
<th>Fe:Se ratio</th>
<th>Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min</td>
<td>10 min</td>
</tr>
<tr>
<td>1:1</td>
<td>hex-FeSe</td>
</tr>
<tr>
<td>1:2</td>
<td>Mixture of Fe$_3$Se$_4$, tet-FeSe, hex-FeSe</td>
</tr>
<tr>
<td>1:4</td>
<td>Fe$_3$Se$_4$</td>
</tr>
</tbody>
</table>

The precursors of interest in this study included iron acetate and diethylammonium diphenyldiselenophosphinate, or DSP (Figure 2.5). Although the iron in Fe$_3$Se$_4$ is mixed valent with one divalent iron (Fe$^{2+}$) and two trivalent irons (Fe$^{3+}$), divalent iron is present in all iron selenide phases of interest, specifically tet-FeSe. Accordingly, a divalent iron precursor was chosen to avoid redox chemistry. The DSP salt provides Se$^{-2}$ and has been shown to be slightly reducing, further supporting stabilization of divalent iron.

![Figure 2.5. Structure of diethylammonium diphenyldiselenophosphinate, DSP.](image)

Precursor preparation is vital in elucidating control for the iron selenide phase. In fact, our first studies involved the preparation of the iron acetate and DSP precursors in the presence of air prior to injection in hot capping ligand. The phases that were primarily observed include hex-FeSe and Fe$_3$Se$_4$ at all precursor ratios and reaction times. A closer look at the literature reports the effects of oxygen-impurities on the synthesis and superconductivity of bulk tet-FeSe.$^{32}$ The authors
found that in the solvothermal synthesis of tet-FeSe, samples prepared in the presence of air introduced oxygen-impurities in the structure (Figure 2.6) resulting in iron deficient materials and ultimately affecting the superconductivity. Although the presence of oxygen impurities within the synthesized iron selenide phases here was not probed, preparing the precursor solution in an inert atmosphere afforded the opportunity to synthesize a wider range of iron selenide phases and structure types.

![Figure 2.6. Structural model of oxygen impurities in tet-FeSe. In the presence of oxygen, an iron vacancy can become occupied by an oxygen atom. Reprinted with permission from Greenfield, J. et.al. Chem. Mater., 2015, 27, 588. Copyright 2015 American Chemical Society.][1]

The precursor ratio was found to be one of the largest contributing factors in establishing phase control of iron selenide. A 1:1 mole ratio of precursors (or 1Fe:2Se) as well as a 1:2 mole ratio (or 1Fe:4Se) typically favored the formation of Fe₃Se₄, whereas a stoichiometric 2:1 mole ratio (or 2Fe:2Se) resulted in FeSe (hexagonal and/or tetragonal). This clearly indicates that an excess of selenium in solution leads to a selenium-rich iron selenide phase Fe₃Se₄. Alternatively, a stoichiometric amount or slight excess of iron will result in the formation of the stoichiometric iron selenide phases, hex-FeSe and tet-FeSe.
Reaction time, or the time allowed post-injection of the precursor solution, was ultimately the deciding factor in elucidating iron selenide phase and structure type control for the preparation of tet-FeSe. At a 1:1 mole ratio of precursors (or 1Fe:2Se), a mixture of tet-FeSe and Fe$_3$Se$_4$ iron selenide phases was observed at reaction times of 5-20 minutes; pure Fe$_3$Se$_4$ was obtained at reaction times of 25-180 minutes (Figure 2.7). With an even greater excess of selenium (1Fe:4Se), Fe$_3$Se$_4$ was observed at reaction times of 5-180 minutes without any observable change in crystallinity.

![Figure 2.7. PXRD of Fe$_3$Se$_4$. Diffraction pattern shown is of sample SEI-157-A obtained after a 30-minute reaction time. Each sample of pure Fe$_3$Se$_4$ displayed as similar pattern.](image-url)
At a 2:1 mole ratio (or 2Fe:2Se), a transition of phases is observed over time, in which the hex-FeSe structure type is favored at shorter reaction times (5 minutes), and the tet-FeSe structure type stabilizes at 20 minutes (Figure 2.8). Based on these observations, tet-FeSe is the thermodynamically favored product under the specific conditions studied. However, it is unclear whether the hex-FeSe is in fact kinetically favored. Given the proposed phase diagram of bulk iron selenide (Figure 2.9), hex-FeSe is favored at lower reaction temperatures (280-300°C). Upon the injection of precursors at room temperature to the capping ligand solution at 330°C, the temperature generally decreases to ~290°C. Because of this temperature drop, it is possible that the hex-FeSe may initially form because it is thermodynamically favored at the immediate post-injection temperature drop. As the temperature establishes equilibrium at 330°C, the tet-FeSe structure type beings to form. The ‘heat-up’ approach could be employed to study the thermodynamically stable product at the post-injection temperature of about 290°C. However, since our interest stemmed in synthesizing tet-FeSe for its superconducting properties, this was not probed.
Figure 2.8. PXRD comparison of time effects. Hex-FeSe (red, SEI-77-A) transitions to tet-FeSe (blue, SEI-89-A) over 20 minutes. A mixture of phases can be seen at intermediate times (15 minutes, in SEI-83-A).
Figure 2.9. Binary phase diagram of iron selenide. Reproduced with permission from the American Physical Society.\textsuperscript{31}

The iron selenide phase, orthorhombic FeSe\textsubscript{2}, can also be synthesized via the hot injection method. Compared to the synthesis of Fe\textsubscript{3}Se\textsubscript{4} using a 1:1 mole ratio of precursors (or 1Fe:2Se) after 60-minute reaction time, replacing oleylamine with a oleylamine/oleic acid capping ligand mixture affords the synthesis of FeSe\textsubscript{2} (Figure 2.10). The peak at 19° can be attributed to an iron oxide phase, Fe\textsubscript{3}O\textsubscript{4}, which may have formed as a result of the presence of oxygen from oleic acid. The use of oleylamine and oleic acid as co-solvents in nanoparticle syntheses is often used to influence morphology,\textsuperscript{13} since oleic acid is a stronger ligand than amine ligands, like oleylamine.\textsuperscript{3} However, one study reports the necessity of an oleylamine/oleic acid mixture for the synthesis of alloyed iron oxide nanoparticles, MFe\textsubscript{2}O\textsubscript{4}, where M = Fe, Co, Mn.\textsuperscript{43} The sole use of oleylamine resulted in low yields, and oleic acid alone resulted in a material that was difficult to characterize. Another report indicates that an oleylamine/oleic acid co-solvent system aided in establishing
phase purity for FeS$_2$ nanomaterials via solvothermal routes.\textsuperscript{17} Therefore, oleic acid may lead to the formation of FeSe$_2$ via the hot injection method.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{pxrd.png}
\caption{PXRD of orthorhombic FeSe$_2$ via the hot injection method. Sample SEI-61-A shows FeSe$_2$ in red, and the peak at 2$\theta$=19$^\circ$ is attributed to Fe$_3$O$_4$.}
\end{figure}

The solvothermal method has also proved to be a viable synthetic route for orthorhombic FeSe$_2$ (Figure 2.11), similar to what has been reported in the literature for FeS$_2$ and FeSe$_2$.\textsuperscript{17,20,21,44–46} Despite the presence of oxygen in the reaction conditions from water, an iron oxide phase is not observed. It is also important to note that only the orthorhombic FeSe$_2$ structure type is observed in both the hot injection and solvothermal routes. According to the literature, the orthorhombic phase is favored at ambient conditions whereas the cubic structure type forms at high temperature.
and pressures\textsuperscript{20,47} and is thus not observed via these low temperature routes. In testing the solvothermal approach as a route to other iron selenide phases, variation of reaction precursor mole ratios, solvent choice, reaction temperature, and/or reaction time, consistently resulted in pure phase FeSe\textsubscript{2} despite the report by Li and coworkers.\textsuperscript{37} It is possible that our specific conditions investigated cannot support the formation of multiple phases of iron selenide, but alternative syntheses were not pursued given the success of the hot injection method approach.

**Figure 2.11. PXRD of orthorhombic FeSe\textsubscript{2} from the solvothermal route.** Sample SEI-92-A shows phase pure FeSe\textsubscript{2} and does not contain oxygen impurities.
2.3.2 Morphology Control of Iron Selenide

Morphology control in nanomaterials has been reported for many systems, but no one approach works for a broad range of materials. In targeting tet-FeSe for its superconductivity, we were largely interested in pursuing morphology control for nanowires because of the direct pathway in which electrons can travel, thereby providing an opportunity to enhance superconductivity in iron selenide. Xia has demonstrated the chemical conversion of nanostructures to conserve morphology.\textsuperscript{48–50} Synthesized selenium nanowires are shown to serve as a template for cation insertion to form Ag\textsubscript{2}Se nanowires. Subsequent cation exchange reactions can also be employed in which CdSe.\textsuperscript{49} The success of cation transformation reactions is largely dependent on small structural changes thereby limiting stress on the structure to maintain wire morphology. Because of the tetragonal structure types of selenium, selenium nanowires could serve as a framework for tet-FeSe nanowires. Therefore, the synthesis of Se nanowires was probed as a possible route for iron selenide nanowires via subsequent cation insertion and/or cation exchange reactions. However, the synthesis of Se nanowires was found to be a delicate method resulting in varied morphologies over several trials (Figure 2.12), from faceted box-like structures approximately 400-500 nm in length to thin wires several hundreds of nm in length. The difference in morphology was found to be related to the cooling process in which the seed Se particles are formed. The initial trials utilized rapid cooling of the resulting solution in an ice bath, whereas the final trial utilized a slower cooling process. Therefore, it is observed that slower cooling can enable 1D growth. By controlling the cooling process even more, the growth of more selenium wires may be achieved, but given the sensitivity of this method, other synthetic routes for morphology control of iron selenide nanostructures were investigated.
Figure 2.12. Characterization of Se nanorods and nanowires. PXRD of SEI-30-A showing Se, SEM of Se nanorods in SEI-7-A (top left inset), and SEM of Se wires and rods in SEI-30-A (top right inset).

Alternatively, morphology control of nanomaterials can be accomplished in the hot injection method by utilizing different capping ligands or combinations of capping ligands in a co-solvent system. The syntheses of nearly all iron selenide compositions discussed in Section 2.3.1 were performed in oleylamine, except that of FeSe₂ which employed an oleylamine/oleic acid mixture. It is also important to note that acetate from the iron acetate precursor may also act as a capping ligand in the synthesis of nanoparticles. In fact, it has been reported that in the synthesis of PbSe nanocrystals, the presence of acetate afforded star-like morphology whereas spherical
particles can be obtained in the absence of acetate. Because we have been able to synthesize a range of iron selenide phases with iron acetate as a precursor, we have not studied other precursors or any effects from the acetate anion as a capping ligand. Also, since the amount of acetate introduced into the reactions is relatively small when compared to other capping ligands, and the steric effects from the smaller acetate molecule are reduced, it can be assumed that acetate does not play a large role in the work demonstrated here.

Therefore, in establishing morphology control, alternative long chain capping ligands were investigated. By introducing a 1:1 mixture of hexadecylamine and oleylamine, morphology control for monodisperse tet-FeSe cubic nanoplatelets of approximately 150 nm across (Figure 2.13) are observed via SEM and TEM. Without hexadecylamine, cubic material is still seen, but other morphologies also exist. It is possible that steric effects result from the sole use of the longer chain oleylamine, whereas a co-solvent system of oleylamine and hexadecylamine reduces steric effects for the formation of monodisperse cubic nanoplatelets. An interesting feature to the nanoplatelets is the observation of what appear to be several stacked layers of nanosheets. Although this is expected given the naturally layered structure of tet-FeSe, additional morphology control for individual or a few sheets is of interest. This may be accomplished via exfoliation through intercalation and could potentially follow the work addressing composition control via doping in Chapter 3.
Figure 2.13. Morphology control of tet-FeSe. (B) TEM image of polydisperse tet-FeSe in SEI-89-A and (B) TEM and SEM (inset) images of cubic nanoplatelets of tet-FeSe approximately 150nm across in SEI-91-A.

Morphology control of Fe$_3$Se$_4$ was also investigated. In this case, precursor mole ratio and reaction time were both contributing factors in the synthesis of monodisperse Fe$_3$Se$_4$ platelets (Figure 2.14). Although pure phase Fe$_3$Se$_4$ is synthesized in the presence of excess selenium, a great excess (1Fe:4Se) results in the material seen in Figure 2.14A, whereas a mole ratio of 1Fe:2Se of reaction times of at least 30 minutes results in the material shown in Figure 2.14B. To account for this difference, it is possible that the large excess of selenium may exist in an amorphous phase, resulting in the polydisperse material observed. Also, reaction time may be critical in the growth of nanoplatelets.
2.3.3 Approaches for Superconducting FeSe

To date, we have demonstrated the ability to control iron selenide phase via the hot injection method for nanomaterials, which can be probed for investigating unique properties related to each phase. Of particular interest is the superconductivity in tet-FeSe. A low field magnetic susceptibility measurement of a synthesized tet-FeSe sample (SEI-91-A) does not show superconductivity. However, measuring superconductivity in our samples may be challenging due to our limited access to the necessary instrumentation and given literature reports regarding the loss of superconductivity in iron selenide samples after three days when exposed to air. There is
the chance that our as-synthesized samples may be superconducting, but superconductivity is lost in transfer and preparation for magnetic measurements.

Given the extreme sensitivity to stoichiometry on superconductivity in tet-FeSe, it is important to establish composition control for Fe$_{1.01}$Se. Iodine has been shown to be effective in the deintercalation of interstitial iron in Fe$_{1+x}$Te via a solid state approach.$^{52}$ We do not know the precise stoichiometry of our as-synthesized tet-FeSe samples, and we acknowledge that the difference between the superconducting stoichiometry and the nonsuperconducting stoichiometry is extremely subtle. Based on the literature, synchrotron X-ray diffraction (SXRD) analysis can be utilized to detect the superconducting Fe$_{1.01}$Se and nonsuperconducting Fe$_{1.03}$Se compositions (Figure 2.15A), indicated by the arrows showing the splitting of some peaks, and ultimately resulting in the lattice parameters shown in Figure 2.15B.$^{53}$

![Figure 2.15. Structural differences between Fe$_{1.01}$Se and Fe$_{1.03}$Se.](image)

(A) SXRD showing the splitting of some peaks in superconducting Fe$_{1.01}$Se, indicated by arrows, and (B) lattice parameters for nominal compositions of Fe:Se between 0.98 and 1.02. Reproduced with permission from John Wiley and Sons.$^{53}$
Therefore, establishing a method in which to control stoichiometry via the deintercalation of iron on the nanoscale is a priority. To test iodine’s ability to remove iron from iron selenide, prepared tet-FeSe was mixed with iodine and heated in a sealed quartz tube at 200°C for 18 hours via a solid-state approach. PXRD analysis (Figure 2.16) indicates the successful removal of iron; however, it can be observed that a large amount of iron was removed, resulting in the formation of a mixed phase system containing Se, FeSe₂, and tet-FeSe.

![Figure 2.16. PXRD analysis after iron deintercalation via solid state methods.](image)

After reaction with iodine, SEI-109-A is a mixture of Se (red), FeSe₂ (blue), and tet-FeSe (black).
Given the scale of the reaction, it is possible that an excess of iodine was employed; however, measuring smaller amounts of iodine via this approach for finer control of composition would be extremely challenging. Also, the kinetics of this reaction on the nanoscale may be faster than those observed in the bulk. As a result, we sought to adapt these methods for a solution phase approach to (1) establish finer control of the amount of iodine used in the reaction and (2) to slow the reaction. Employing a dilute solution of iodine can enable finer control over the amount of iodine introduced in the reaction. Also, lower temperatures can slow the reaction for finer control over composition. As such, a prepared sample of tet-FeSe was dispersed in hexanes and mixed with a dilute solution of iodine in hexanes at room temperature. Three individual samples were prepared to target varying amounts of iron deintercalation. PXRD analysis of the isolated materials show Se with some tet-FeSe (Figure 2.17), but all samples showed poor crystallinity. Although a smaller amount of iodine was employed via this solution-phase approach, fine tune control over the nanomaterial composition continues to be a challenge.
Figure 2.17. PXRD analysis after iron deintercalation via solution-phase approach. After reaction with iodine, SEI-245-A is a mixture of Se (red) and tet-FeSe (blue).

2.4 Conclusion

In conclusion, we report the first example demonstrating control of the FeSe$_2$, Fe$_3$Se$_4$, FeSe iron selenide phases as well as precise control of the tet-FeSe and hex-FeSe structure types with small, controlled changes to the reaction conditions via the hot injection method. Of the reaction conditions investigated, precursor mole ratio largely influenced the Fe$_3$Se$_4$ in selenium-rich conditions and the FeSe phase in iron-rich conditions. Employing a co-solvent system of oleylamine and oleic acid favored the formation of FeSe$_2$. Ultimately, reaction time was found to be the factor elucidating control for FeSe structure type, where hex-FeSe is favored at shorter
reaction times (5 minutes) which converts to the thermodynamically stable tet-FeSe at reaction times of at least 20 minutes. Intermediate reaction times afford a mixture of the hexagonal and tetragonal structure types. This work also demonstrates the ability to control morphology for tet-FeSe cubic nanoplatelets by using an appropriate capping ligand mixture of oleylamine and hexadecylamine. Although the synthesized tet-FeSe nanomaterials do not show superconductivity, establishing composition control for Fe$_{1.01}$Se via the deintercalation of interstitial iron has proved to be challenging on the nanoscale. This is largely due to the subtle differences between the superconducting and nonsuperconducting compositions. Additional approaches regarding composition control for inducing superconductivity in tet-FeSe via doping are discussed in Chapter 3.
CHAPTER 3. SYNTHETIC APPROACHES TO INTERCALATED IRON SELENIDE NANOSTRUCTURES

3.1 Introduction

Transition metal chalcogenides, like FeSe, generally show a layered structure. Since the interaction between layers is via weak chemical bonding or van der Waals forces, layered chalcogenides are of interest as hosts for chemical intercalation (Figure 3.1). Alkali metals, alkaline earth metals, rare earth metals, and other molecules or compounds can be intercalated between the layers of the host structure, thereby serving as a ‘carrier reservoir’ between adjacent conducting layers. As a result, chemical intercalation has proved to be an effective means of tuning physical and chemical properties of interest in creating new functional materials.\(^7\)

![Figure 3.1. Schematic representation of intercalation in tet-FeSe. Reproduced with permission from Springer.\(^5^4\)](image)

After the discovery of superconductivity in tet-FeSe (\(T_c=8.5\)K)\(^2^6\) and the effects of pressure on enhancing the superconductivity to \(T_c=37\)K,\(^2^7\) chemical intercalation has been studied as a means of further increasing the superconducting critical temperature. To date, it has been shown that, without pressure, sodium and potassium intercalation in the bulk results in \(\text{Na}_x\text{Fe}_{2-y}\text{Se}_2\) and \(\text{K}_x\text{Fe}_{2-y}\text{Se}_2\), respectively, with critical temperatures in the range of 30-46K.\(^5^5-5^8\) Other alkali metals
have been intercalated in large single crystals of iron selenide, such as Cs$_x$Fe$_2$Se$_2$ with $T_c = 27$-30K$^{57,59}$ and Rb$_x$Fe$_2$Se$_2$ with $T_c = 32$K.$^{60}$ Synthetically, these single crystals are grown from the respective elements via a solid state approach at high temperatures in the range of 700-1000°C.

Alternatively, the low temperature ammonothermal route has been reported for the synthesis of bulk A$_x$Fe$_2$Se$_2$ (A = Li, Na, K, Ba, Sr, Ca, Yb, and Eu) with critical temperatures up to 46K (Figure 3.2).$^{58}$ In this approach, pure metal is dissolved in liquid ammonia (T=-78°C) and mixed with a pre-synthesized iron selenide sample for incorporation. Here, alkali, alkaline earth, and even rare earth metals are shown to intercalate iron selenide based on the metal’s solubility in liquid ammonia.

![Figure 3.2. Enhanced superconductivity in A$_x$Fe$_2$Se$_2$ via an ammonothermal approach. Reproduced with permission from Nature Publishing Group.$^{58}$](image)

Although the superconductive shielding fractions, or the percentage of material that is superconducting, are quite low when compared to large single crystals, this method provides a low temperature route for intercalating iron selenide. As a result, lithium has received considerable
attention in forming molecular spacer layers with ammonia\textsuperscript{28,29} or pyridine.\textsuperscript{61} For instance, Li\textsubscript{x}(NH\textsubscript{2})\textsubscript{y}(NH\textsubscript{3})\textsubscript{1-x}Fe\textsubscript{2}Se\textsubscript{2} exhibits superconductivity at 43K, indicating the possibility of exploring molecular intercalates for enhancing superconductivity in iron selenide.\textsuperscript{28}

Upon the intercalation of metal ions into the tet-FeSe structure, the distance between FeSe layers has been observed to increase from 5.52Å to 6.99-7.64Å, in which metals with larger radii result in a larger interlayer distance, and the lattice parameter, $a$, expands from 3.77Å to 3.88-3.96Å. A structural configuration change is also observed from a primitive tetragonal lattice to a body-centered tetragonal lattice.\textsuperscript{7} Thus, intercalation can be characterized by their unique diffraction patterns (Figure 3.3) which have been reported for several metals.\textsuperscript{58}

Although intercalated iron selenide has been reported in large single crystals and the bulk, superconducting A\textsubscript{x}Fe\textsubscript{2-\text{\textsubscript{y}}}Se nanomaterials have not been reported. Therefore, given our cubic nanoplatelets containing several individual layers of tet-FeSe, we are interested in the intercalation chemistry of these materials for the possibility of isolating a superconducting material as well as in studying the synthetic conditions and routes for the intercalation of iron selenide nanomaterials.
Figure 3.3. X-ray diffraction patterns for A\textsubscript{x}Fe\textsubscript{2}Se\textsubscript{2}. Reproduced with permission from Nature Publishing Group.\textsuperscript{58}

3.2 Experimental Section

3.2.1 General Information

Calcium acetate, calcium chloride, hexadecylamine (HDA), iron (II) acetate, \textit{n}-butyllithium (\textit{n}-BuLi), oleylamine (OLA, 70%), potassium acetate, potassium metal, potassium tert-butoxide, sodium acetate, and sodium metal were purchased from Sigma Aldrich. Ethanol and hexanes were purchased from Fisher Scientific. Sodium oleate was obtained from Strem Chemicals. Ammonia was purchased from Praxair. All chemicals were used as received. Diethylammonium diphenyldiselenophosphinate (DSP) and potassium
diphenyldiselenophosphinate (KDSP) were prepared as previously described in Section 2.2.1, replacing diethylamine with potassium tert-butoxide in KDSP.\textsuperscript{40} Nanomaterials of tet-FeSe were prepared as described in Section 2.2.3.

X-ray powder diffraction patterns were obtained using a Rigaku Ultima IV X-Ray powder diffractometer with Cu Kα radiation and a DTex detector. SEM images and energy dispersive X-ray spectroscopy (EDX) were obtained with a Zeiss SUPRA 55-VP Scanning Electron Microscope at an acceleration voltage of 9-20 kV with an in-lens detector. High resolution TEM was performed with a JEOL JEM 2100F Field Emission Gun Transmission Electron Microscope at 200 kV at the University of Maryland Nanoscale Imaging Spectroscopy and Imaging Laboratory.

3.2.2 Approaches for Alkali and Alkaline Earth Metal Intercalation

Alkali metal intercalation via ammonothermal method, SEI-234-A and SEI-241-A. In the glove box, a prepared sample of tet-FeSe (SEI-237-A, 55.5 mg, 0.4117 mmol) and alkali metal (Na or K, 0.2 mmol) were added to a schlenk flask equipped with a stir bar. Once sealed, the flask was evacuated, flushed with NH\textsubscript{3}(g) and then slowly lowered into a dewar filled with liquid nitrogen. When NH\textsubscript{3}(l) (15 mL) had condensed, the liquid nitrogen dewar was replaced with dry ice/acetone bath and a blue color indicative of alkali metal dissolution was observed. The resulting mixture stirred ~3 hours and NH\textsubscript{3}(g) was allowed to bubble through the schlenk line, revealing a black material. PXRD analysis of SEI-234-A showed tet-FeSe (PDF#01-085-0735) and Se (PDF#01-073-0465): 23.338°, 3.8084Å; 28.420°, 3.1379Å; 29.538°, 3.0217Å; 37.162°, 2.4174Å; 43.460°, 2.0806Å; 47.143°, 1.9263Å; 47.882°, 1.8982Å; 56.682°, 1.6226Å. PXRD analysis of SEI-241-A showed pure phase Se (PDF#01-073-0465): 23.297°, 3.8151Å; 29.498°, 3.0256Å; 41.134°, 2.1927Å; 43.441°, 2.0814Å; 45.157°, 2.0063Å; 51.557°, 1.7712Å; 64.922°, 1.4352Å.
General reaction for sodium intercalation via hot injection method. A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. The capping ligand or co-solvent mixture and sodium precursor (0.3 mmol) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and the mixture refluxed at 330°C. Meanwhile, the precursor solution was prepared in the glove box by dissolving iron acetate (0.6 mmol) and DSP (0.3 mmol) in oleylamine (5.0 mL). The precursor solution was injected into the hot capping ligand solution, resulting in a black color. The reaction mixture heated 20-60 minutes and then slowly cooled to room temperature. The resulting mixture was washed with a mixture of hexanes and ethanol several times, centrifuged at 4000 rpm for 10 minutes and the supernatant was discarded, resulting in black product. PXRD was obtained to show tet-FeSe (PDF#01-085-0735), hex-FeSe (PDF#01-071-4479), and another tet-FeSe phase (PDF#01-073-6936), specifically for the representative sample SEI-249-A: 15.859°, 5.5835Å; 28.400°, 3.1401Å; 32.100°, 2.7861Å; 35.280°, 2.5419Å; 37.159°, 2.4176Å; 41.921°, 2.1533Å; 47.141°, 1.9263Å; 47.880°, 1.8983Å; 50.120°, 1.8186Å; 56.664°, 1.6231Å.

General reaction for potassium intercalation via hot injection method. A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. The capping ligand or co-solvent mixture and potassium precursor\(^a\) (0.3 mmol) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and the mixture refluxed at 330°C. Meanwhile, the precursor solution was prepared in the glove box by dissolving iron acetate (0.6 mmol) and DSP (0.3 mmol) in oleylamine (5.0 mL). The precursor solution was injected into the hot capping ligand solution, resulting in a black color. The reaction

\(^a\) When the KDSP salt was used as both the potassium and selenium source, the capping ligand solution was degassed in the absence of a separate potassium source.
mixture heated 30-60 minutes and then slowly cooled to room temperature. The resulting mixture was washed with a mixture of hexanes and ethanol several times, centrifuged at 4000 rpm for 10 minutes and the supernatant was discarded, resulting in black product. PXRD was obtained to show a mixture of Se (PDF#00-006-0362), tet-FeSe (PDF#01-085-0735), and KFeSe₂ (PDF#01-071-2104), specifically for the representative sample SEI-253-A: 15.177°, 5.8330Å; 15.920°, 5.5624Å; 23.220°, 3.8276Å; 28.400°, 3.1401Å; 29.400°, 3.0356Å; 35.219°, 2.5462Å; 40.979°, 2.2006Å.

**General reaction for calcium intercalation via hot injection method.** A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. The capping ligand or co-solvent mixture and calcium precursor (0.3 mmol) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and the mixture refluxed at 330°C. Meanwhile, the precursor solution was prepared in the glove box by dissolving iron acetate (0.6 mmol) and DSP (0.3 mmol) in oleylamine (5.0 mL). The precursor solution was injected into the hot capping ligand solution, resulting in a black color. The reaction mixture heated 20-60 minutes and then slowly cooled to room temperature. The resulting mixture was washed with a mixture of hexanes and ethanol several times, centrifuged at 4000 rpm for 10 minutes and the supernatant was discarded, resulting in black product. PXRD was obtained to show tet-FeSe (PDF#01-085-0735) and hex-FeSe (PDF#01-071-4479), specifically for the representative sample RA138: 15.900°, 5.5692Å; 28.481°, 3.1314Å; 32.078°, 2.7880Å; 37.241°, 2.4124Å; 47.220°, 1.9233Å; 48.019°, 1.8931Å; 55.420°, 1.6566Å; 56.859°, 1.6180Å; 70.339°, 1.3373Å.
**Lithium intercalation.** In the glove box, a prepared sample of tet-FeSe cubic plates (SEI-105-A, 19.9 mg, 0.1476 mmol) was added to a glass centrifuge tube followed by n-BuLi (2.0 mL) and stirred at room temperature for 20 hours. The resulting material was allowed to settle and the supernatant was decanted. Hexanes (2.0 mL) was added, the mixture stirred, and once the material had settled, the supernatant was removed via decantation. This washing process was repeated several times. The resulting black material was isolated and labeled SEI-158-A. PXRD analysis revealed an amorphous material.

**3.3 Results and Discussion**

In Wang’s report, the ammonothermal route is an effective method for the preparation of intercalated iron selenide materials with higher critical temperatures. In this approach, the liquid ammonia acts both as a solvent that allows the iron selenide host to absorb solvated electrons, as well as a spacer molecule that facilitates the intercalation process. Given its success in the bulk, we adapted the ammonothermal route for the intercalation of our synthesized tet-FeSe nanomaterials. Here, prepared tet-FeSe nanomaterial is exposed to an alkali metal dissolved in liquid ammonia. In particular, sodium and potassium were investigated as potential intercalates for Na$_x$Fe$_2$$_y$Se$_2$ and K$_x$Fe$_2$$_y$Se$_2$, respectively. In our adaptation, the reaction duration was kept to a few hours (~2-3 hours) as opposed to several days since the diffusion path is much smaller on the nanoscale than in the bulk. However, PXRD analysis of the resulting powders indicate the presence of selenium with some tet-FeSe from the potassium reaction (Figure 3.4). It is unclear how iron has been removed from the material, but we can conclude that potassium and sodium have not intercalated iron selenide nanomaterials via the ammonothermal method. In fact, intercalation of iron selenide nanomaterials may require alternative synthetic approaches.
Figure 3.4. PXRD analysis from ammonothermal reactions. (A) SEI-234-A from the reaction of tet-FeSe with potassium and (B) SEI-241-A from the reaction of tet-FeSe with sodium.
As an alternative to the ammonothermal route, we sought to synthesize intercalated iron selenide nanostructures *in situ* via a modified hot injection approach. To do so, an alkali metal salt was introduced into the hot injection method for the synthesis of tet-FeSe nanomaterials. In the case of sodium-doped iron selenide, sodium acetate and sodium oleate were investigated as potential dopant precursors (Table 3.1). Despite precursor ratio, capping ligand(s), or reaction time, the resulting material showed a mixture of tet-FeSe, hex-FeSe, and another tet-FeSe phase (Figure 3.5). Although this second tet-FeSe phase has not been observed by us previously, the cell parameter $c = 4.73\text{Å}$ is smaller than that of the other tet-FeSe ($c = 5.518\text{Å}$). This is opposite of what is expected following the intercalation of sodium. In fact, intercalation should increase the interlayer distance, thereby increasing the lattice parameter, $c$. Detecting the presence of sodium from EDX proved to be challenging, since the peaks corresponding to sodium should appear in an identical spot to those of copper from the SEM sample holder.

**Table 3.1. Reaction conditions for Na$_x$Fe$_{2-y}$Se.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na-source</th>
<th>Na:Fe:Se ratio</th>
<th>Capping ligand/solvent</th>
<th>Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>249</td>
<td>Sodium acetate</td>
<td>1:1:1</td>
<td>HDA/oleylamine</td>
<td>20 min</td>
</tr>
<tr>
<td>248</td>
<td>Sodium acetate</td>
<td>1:1:1</td>
<td>HDA/oleylamine</td>
<td>30 min</td>
</tr>
<tr>
<td>250</td>
<td>Sodium acetate</td>
<td>2:1:1</td>
<td>HDA/oleylamine</td>
<td>30 min</td>
</tr>
<tr>
<td>247</td>
<td>Sodium acetate</td>
<td>1:1:1</td>
<td>HDA/oleylamine</td>
<td>1 hr</td>
</tr>
<tr>
<td>260</td>
<td>Sodium oleate</td>
<td>1:1:1</td>
<td>Oleylamine</td>
<td>30 min</td>
</tr>
</tbody>
</table>
Figure 3.5. PXRD analysis from sodium-doped FeSe reaction. Representative sample, SEI-249-A, shows tet-FeSe (red), hex-FeSe (blue), and another tet-FeSe (black).

Potassium-doped iron selenide was also investigated via a modified hot injection approach, in which potassium acetate and the potassium salt of the DSP ligand (KDSP) were investigated as potential dopant precursors (Table 3.2). Here, the KDSP is employed as both the potassium and selenium precursor, while limiting the presence of other ions in solution. Although this puts restrictions on testing various concentrations of potassium in the prepared material, the goal here is to study the ability to intercalate potassium in tet-FeSe nanomaterials.
Table 3.2. Reaction conditions for $\text{K}_x\text{Fe}_{2-y}\text{Se}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>K-source</th>
<th>Capping ligand/solvent</th>
<th>Reaction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>252</td>
<td>KDSP</td>
<td>HDA/oleylamine</td>
<td>30 min</td>
</tr>
<tr>
<td>253</td>
<td>KDSP</td>
<td>Oleylamine</td>
<td>30 min</td>
</tr>
<tr>
<td>255</td>
<td>KDSP</td>
<td>Oleylamine</td>
<td>1 hr</td>
</tr>
<tr>
<td>256</td>
<td>Potassium acetate</td>
<td>Oleylamine</td>
<td>1 hr</td>
</tr>
</tbody>
</table>

Based on the reactions performed with KDSP, PXRD analysis of all samples reveal a mixture of selenium, tet-FeSe, and KFeSe$_2$ (Figure 3.6). SEM reveals polydisperse material with some nanowire morphology and some nanoparticle formations. Although in small quantities, EDX confirms the presence of potassium, in addition to iron and selenium in the nanoparticle formations (Figure 3.7), whereas selenium is predominantly detected in the nanowire formation. This indicates the growth of selenium nanowires as well as the incorporation of potassium into an iron selenide phase. The reaction employing potassium acetate revealed a mixture of selenium and tet-FeSe, with possibly a second phase of tet-FeSe (Figure 3.8); however, EDX of this sample also reveals the presence of potassium, similar to that in Figure 3.7. In comparing the results from both sodium and potassium, it appears that potassium may be better incorporated in iron selenide. In fact, the literature reports that in the bulk synthesis of $(\text{Na}_x\text{K}_y)\text{Fe}_2\text{Se}_2$ in a flux method, potassium is more preferred than sodium as an intercalate, although the reason for this is unclear.$^{62}$
Figure 3.6. PXRD analysis from potassium-doped FeSe reaction using KDSP. Representative sample, SEI-253-A, shows Se (black circle), tet-FeSe (blue asterisk) and KFeSe$_2$ (red line).

Figure 3.7. EDX spectrum indicating the presence of potassium in SEI-253-A.
Figure 3.8. PXRD analysis from potassium-doped FeSe reaction using potassium acetate. Representative sample, SEI-256-A, shows Se (red), tet-FeSe (blue), and a second tet-FeSe phase (black).

The intercalation chemistry was also similarly investigated with calcium salts – calcium chloride and calcium acetate. The reaction utilizing calcium chloride results in a mixture of tet-FeSe and hex-FeSe; however, a sharp peak is also observed at $\theta=10^\circ$ (Figure 3.9), which matches the expected (002) peak for Ca$_{0.5}$Fe$_2$Se$_2$ (Figure 3.3). This peak may be indicative of the incorporation of some calcium in iron selenide, and EDX measurements could reveal the presence of calcium. Although this sample is not phase-pure, it is possible that a longer reaction time is needed for such intercalation reactions, much longer reaction times than those discussed in elucidating structure type control for tet-FeSe in Chapter 2. It is also important to note that this
peak at $2\theta=10^\circ$ is not observed in the reaction employing calcium acetate, indicating that the counter ion matters. Additional calcium salts with differing anions should also be investigated.

**Figure 3.9. PXRD analysis from calcium-doped FeSe reaction using calcium chloride.** Representative sample, RA-138, shows tet-FeSe (red) and hex-FeSe (blue). The peak at $2\theta=10^\circ$ may be $\text{Ca}_{0.5}\text{Fe}_2\text{Se}_2$.

Lithium intercalation in iron selenide was also studied according to methods reported for intercalation and exfoliation of several layered transition metal dichalcogenide systems.$^{63-65}$ By stirring prepared nanosheets of the layered transition metal dichalcogenide in n-butyllithium, lithium can act as an intercalate between the layers. We adapted these methods using a prepared sample of tet-FeSe nanoplates; however, an amorphous material was obtained.
3.4 Conclusion

Because of the extreme sensitivity of superconductivity to stoichiometry in iron selenide, intercalation of the naturally layered tetragonal material may provide a route to synthesizing superconducting tet-FeSe nanomaterials via the hot injection method. The ammonothermal route has been shown to be an effective method for intercalation in the bulk; however, efforts to synthesize $A_xFe_{2-y}Se_2$, where $A = Na$ or $K$, result in the formation of selenium or reduced crystallinity. Alternatively, we sought to synthesize metal-doped iron selenide directly in the hot injection method. The metals of interest included potassium, sodium, and calcium. Analysis of the resulting materials indicates the presence of potassium; however, other iron selenide phases exist. Also, a shift in 2θ is observed in the reaction utilizing calcium chloride for calcium incorporation. This shift in the diffraction peaks matches what is expected for Ca$_{0.5}$Fe$_2$Se$_2$; however, the material is not phase pure. Additional control is needed in these reactions to establish phase control for the materials containing the alkali or alkaline earth metal of interest. Possible conditions influencing composition may include longer reaction times and/or capping ligands.
CHAPTER 4. SYNTHETIC APPROACHES TO SAMARIUM CHALCOGENIDE MATERIALS

4.1 Introduction

The rare earth chalcogenides of samarium sulfide, SmS, and samarium selenide, SmSe, have received considerable interest as a result of changes in the samarium valency when exposed to external parameters such as pressure and temperature. Specifically, at room temperature and zero pressure, SmS is a semiconductor of the NaCl cubic structure with indirect and direct band gaps of 90 mEV and 0.4 eV, respectively. Upon the addition of modest pressure (0.65 GPa), SmS undergoes an abrupt, discontinuous isostructural transition (Figure 4.1A), resulting in a decrease in the resistivity, lattice constant, and a significant volume collapse of nearly 15%. This transition is coupled with a change in color from black Sm$^{2+}$ to the mixed valent (average valency of +2.6 to +2.8, depending on the method) metallic golden phase and is attributed to the promotion of a 4$f$ electron to the 5$d$ conduction band. Upon additional pressure, samarium becomes fully trivalent, transitioning to the CsCl cubic structure type. Similarly, SmSe also exhibits an isostructural transition (Figure 4.1B); however, the transition in SmSe is continuous and reversible resulting in an initial volume collapse of 6.8%. Not only does pressure affect the structure and electronic properties of SmX, but it has also been reported to affect the magnetic properties of SmS which are sensitive to samarium valency. As a result, these isostructural transitions based on samarium valency in samarium monochalcogenides are of interest for technological applications in spintronics and spin filtering devices, combining both transport and magnetic properties. In particular, the continuous and reversible transition observed in SmSe make it a promising candidate in piezoresistive devices which are generally used to measure mechanical stress. A piezoresistor is a material that exhibits
an increased resistance when pressure is applied, and silicon is typically used in such devices. However, phase pure thin films of SmSe have been reported to exhibit ‘giant’ piezoresistive responses when compared to silicon.\textsuperscript{71}

![Figure 4.1. Pressure-Volume relationship for SmS and SmSe.](image)

(A) At 0.65 GPa, SmS undergoes an abrupt isostructural transition from ‘fcc1’ to ‘fcc2’, whereas (B) SmSe exhibits a continuous transition. Reproduced with permission from Elsevier.\textsuperscript{74}

However, as with transition metal chalcogenides and given the subtle transition between Sm\textsuperscript{2+} and Sm\textsuperscript{3+}, multiple phases of samarium chalcogenides exist. Stable known phases include SmX (face centered cubic), Sm\textsubscript{3}X\textsubscript{4} (body centered cubic), and Sm\textsubscript{2}X\textsubscript{3} (orthorhombic), where X = S or Se. It is important to note that SmX contains Sm\textsuperscript{2+}, whereas Sm\textsubscript{2}X\textsubscript{3} is trivalent, and Sm\textsubscript{3}X\textsubscript{4} is mixed valent (Sm\textsuperscript{2+} and Sm\textsuperscript{3+}). Samarium chalcogenide systems have not been extensively studied, particularly on the nanoscale. Our interest in studying these samarium chalcogenide systems is natural given the extensive synthetic work performed in our group on the europium chalcogenide systems that exhibit similar phases and structure types.

Although, the phase diagram for bulk samarium selenide has been reported (Figure 4.2)\textsuperscript{75} and the phase diagram of samarium sulfide has only been partially established,\textsuperscript{76,77} the synthesis
of these materials is energy intensive. Typically, elemental precursors are utilized via solid state methods at high temperatures. Therefore, it would be advantageous to develop low temperature routes which may require alternative precursors. In particular, solution soluble precursors are necessary for the synthesis of controlled nanoparticles, and the synthesis of samarium chalcogenide nanomaterials is of interest for further fine-tuning their electronic and/or magnetic properties of interest.

**Figure 4.2. Samarium selenide phase diagram.** Reproduced with permission from Springer.\textsuperscript{75}  

Herein, efforts to synthesize samarium chalcogenide nanomaterials are presented, indicating the challenges in isolating the samarium composition, SmS or SmSe, which has proven to be difficult to stabilize. Precursors and reaction conditions will be discussed, evaluating the factors favoring and/or limiting the formation of samarium chalcogenide materials for composition control.
4.2 Experimental Section

4.2.1 General Information

Acetonitrile (anhydrous), bis(trimethylsilyl)sulfide ((TMS)$_2$S), borane t-butyl amine complex (TBAB), diphenyl diselenide, di-t-butyl disulfide (tBuSS'Bu), dodecylamine, hexadecylamine (HDA, 98%), isopropyl isothiocyanate, octadecene (ODE, 90%) oleylamine (OLA, 70%), samarium diiodide (anhydrous), sodium sulfide, and toluene were purchased from Sigma-Aldrich. Samarium (III) acetate hydrate was obtained from Strem Chemicals. Hydrogen sulfide (5% in 95% nitrogen) was purchased from Praxair. Ethanol and hexanes were obtained from Fisher Scientific. All chemicals were used as received. Diethylammonium diphenyldiselenophosphinate (DSP) and diethylammonium diphenylthiophosphinate (DTP) were prepared as previously reported$^{40}$ (Section 2.2.1), using selenium or sulfur powder, respectively. The substituted thiourea, 1-dodecyl-3-isopropylthiourea, was prepared as reported.$^{78}$ In brief, a solution of dodecylamine in toluene was added to a solution of isopropyl isothiocyanate in toluene and briefly stirred. Removal of the solvent under vacuum afforded a white powder. X-ray powder diffraction patterns were obtained using a Rigaku Ultima IV X-Ray powder diffractometer with Cu Kα radiation and a DTex detector. SEM images were taken with a Zeiss SUPRA 55-VP Scanning Electron Microscope at an acceleration voltage of 9-20 kV with an in-lens detector. High resolution TEM and EDX were performed with a JEOL JEM 2100F Field Emission Gun Transmission Electron Microscope at 200 kV at the University of Maryland Nanoscale Imaging Spectroscopy and Imaging Laboratory.
4.2.2 Solid State Approaches for Samarium Chalcogenide Materials

**Sm$_2$O$_2$S, SEI-127-A.** Under inert atmosphere, samarium diiodide (0.1107 g, 0.2739 mmol) and sodium sulfide (0.0215 g, 0.2755 mmol) were loaded into a graphite boat which was then placed in a horizontal furnace tube with an opening on one end. In the furnace, the sealed tube was placed under vacuum, heated at 700°C for 3 hours, and then slowly cooled to room temperature. PXRD analysis of the tan powder showed pure phase Sm$_2$O$_2$S (PDF #01-070-7454): 25.777°, 3.4533Å; 26.380°, 3.3758Å; 29.596°, 3.0159Å; 33.499°, 2.6729Å; 37.741°, 2.3817Å; 46.580°, 1.9482Å; 48.759°, 1.8661Å; 54.385°, 1.6856Å; 56.246°, 1.6344Å.

**Sm$_3$S$_4$, SEI-134-A.** Under inert atmosphere, samarium diiodide (0.1110 g, 0.2746 mmol) and DTP (0.0890 g, 0.2751 mmol) were loaded into a half graphite boat which was then placed in a horizontal furnace tube open on both ends. The furnace tube was quickly evacuated and then heated to 700°C under flowing hydrogen sulfide. After 3 hours, the tube slowly cooled to room temperature. PXRD analysis of the orange powder showed pure phase Sm$_3$S$_4$ (PDF #01-071-0433): 16.092°, 5.5034Å; 28.561°, 3.1227Å; 37.320°, 2.4075Å; 47.320°, 1.9195Å; 47.982°, 1.8945Å; 55.517°, 1.6539Å; 56.880°, 1.6174Å.

**SmS by annealing Sm$_2$O$_2$S, SEI-128-A.** Under inert atmosphere, a prepared sample of Sm$_2$O$_2$S was loaded into a half graphite boat which was then placed in a horizontal furnace tube with openings on both ends. The furnace tube was quickly evacuated, and the temperature was set to 700°C for 3 hours under flowing hydrogen sulfide. PXRD analysis of the gray powder showed a mixture of SmS (PDF #01-077-3343) and Sm$_2$O$_2$S (PDF #01-070-7454): 26.439°, 3.3683Å; 29.581°, 3.0174Å; 31.159°, 2.8681Å; 37.724°, 2.3827Å; 46.600°, 1.9474Å; 48.760°, 1.8661Å; 54.419°, 1.6846Å; 56.198°, 1.6355Å; 61.519°, 1.5062Å; 75.958°, 1.2517Å.
**Sm$_3$S$_4$ by annealing Sm$_2$O$_2$S, SEI-230-A.** Under inert atmosphere, a prepared sample of Sm$_2$O$_2$S was loaded into a half graphite boat which was then placed in a horizontal furnace tube with openings on both ends. The furnace tube was quickly evacuated, and the temperature was set to 1000°C for 5 hours under flowing hydrogen sulfide. PXRD analysis of the golden yellow powder showed pure phase Sm$_3$S$_4$ (PDF #01-071-0433): 25.619°, 3.4744Å; 33.319°, 2.6869Å; 39.681°, 2.2695Å; 47.919°, 1.8969Å; 50.419°, 1.8085Å; 55.198°, 1.6627Å; 68.159°, 1.3747Å; 72.202°, 1.3073Å.

4.2.3 Solution-Phase Approaches for Samarium Chalcogenide Nanomaterials

**General reaction for samarium sulfide using a Sm$^{3+}$ precursor.** A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. Samarium acetate (0.4 mmol) and capping ligand/solvent solution (10.0 mL total volume) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and allowed to reflux. Meanwhile, in the glove box, a stoichiometric amount of sulfur precursor (DTP, thiourea, substituted thiourea, or 'BuSS'Bu) was dissolved in OLA (5.0 mL). The sulfur solution was injected into the hot capping ligand solution and heated at least 1 hour. Once cooled, the resulting product was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD of representative sample, SEI-191-A, showed a poorly crystalline sample indexed to SmS (PDF #01-077-3343) and Sm$_3$S$_4$ (PDF #01-071-0433): 26.819°, 3.3215Å; 32.940°, 2.7170Å; 46.659°, 1.9451Å; 55.080°, 1.6660Å; 67.646°, 1.3839Å.

**General reaction for samarium sulfide using a Sm$^{2+}$ precursor.** In the glove box, a three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. A samarium diiodide solution in acetonitrile (0.05 M, 6.0 mL) was added to OLA (15.0 mL). Once
sealed, the apparatus was attached to the Schlenk line, briefly degassed at 110°C, purged with nitrogen, and heated to 150°C. Meanwhile, in the glove box, (TMS)$_2$S (0.05 mL) was added to ODE (5.0 mL) in a Schlenk flask. This flask was attached to the Schlenk line, purged with nitrogen, and the (TMS)$_2$S solution was carefully injected into the hot capping ligand solution. The reaction mixture heated 1 hour and then slowly cooled to room temperature. The resulting product was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. All glassware containing (TMS)$_2$S was treated with water and bleach to limit odorous hydrogen sulfide formation and exposure. PXRD of SEI-203-A and SEI-263-A were obtained to showed crystalline samples that could not be identified: 19.079°, 4.6479Å; 28.918°, 3.0850Å; 29.281°, 3.0476Å; 38.993°, 2.3080Å; 49.380°, 1.8441Å; 60.239°, 1.5350Å. In a similar reaction heated to 300°C, PXRD analysis of SEI-205-A showed a mixture of SmS (PDF #01-077-3343) and Sm$_2$O$_2$S (PDF #01-070-7454): 29.421°, 3.0334Å; 31.438°, 2.8433Å; 45.098°, 2.0087Å; 54.740°, 1.6755Å; 65.768°, 1.4188Å; 74.667°, 1.2702Å.

**General reaction for samarium selenide.** A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. Samarium acetate (0.4 mmol) and capping ligand/solvent solution (10.0 mL total volume) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and allowed to reflux at 330°C. Meanwhile, the Se-precursor solution was prepared in the glove box by dissolving the selenium precursor (0.2 mmol) in OLA (5.0 mL). The Se-solution was injected into the hot capping ligand solution. The reaction mixture heated 30-180 minutes and then slowly cooled to room temperature. The resulting purple product was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD of a representative sample, SEI-149-A, showed a poorly
crystalline sample indexed to Sm$_3$Se$_4$ (PDF #01-071-3415): 29.857°, 2.9901 Å; 32.241°, 2.7743 Å; 46.274°, 1.9604 Å.

Samarium selenide using borane $t$-butyl amine complex, SEI-213-A. A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. Samarium acetate (0.5 mmol), OLA (7.5 mL), and HDA (1.9554 g) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and allowed to reflux at 330°C. Meanwhile, the Se-precursor solution was prepared in the glove box by dissolving diphenyl diselenide (0.2 mmol) and TBAB (1.5 mmol) in OLA (5.0 mL). The Se-solution was injected into the hot capping ligand solution. The reaction mixture heated 1 hour and then slowly cooled to room temperature. The resulting purple product was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD was obtained to show a poorly crystalline sample indexed to SmSe (PDF #01-077-3414) and Sm$_3$Se$_4$ (PDF #01-077-3415): 26.298°, 3.3862 Å; 29.302°, 3.0455 Å; 31.879°, 2.8049 Å; 45.819°, 1.9788 Å; 55.000°, 1.6682 Å; 66.842°, 1.3985 Å.

4.3 Results and Discussion

4.3.1 Solid State Approaches for Samarium Chalcogenide Materials

The synthesis of bulk samarium chalcogenides with composition control has been reported and is based on the reaction of stoichiometric amounts of elemental samarium and sulfur or selenium powder in evacuated quartz tubes at temperatures exceeding 1000 K. However, these precursors and reaction conditions pose several challenges for the synthesis of nanomaterials. First, the elemental precursors are not soluble in the capping ligands and solvents used in solution-phase nanoparticle routes. Also, the reaction between elemental precursors relies on redox chemistry.
We recognize that this may also be the case via solution phase approaches given the limited availability of samarium precursors, but one of the opportunities for solution synthesis is to utilize a divalent samarium precursor. Although it is possible to synthesize samarium dihalides, we used the commercially available Sm$^{2+}$ salt, samarium diiodide. The thermal decomposition of samarium diiodide was tested via solid state approaches in the presence of a stoichiometric amount of sulfur precursor (S$^2$) – either sodium sulfide or DTP – resulting in the synthesis of an oxysulfide phase, Sm$_2$O$_2$S. Here, divalent samarium has been oxidized to the unfavorable trivalent state, demonstrating the significantly more oxophillic nature of samarium when compared to europium chalcogenide systems. With the addition of a reducing agent, hydrogen sulfide, the mixed valent Sm$_3$S$_4$ composition is observed. Intermediate conditions utilizing hydrogen sulfide as both a sulfur source and a reducing agent results in a mixture of Sm$_2$O$_2$S and Sm$_3$S$_4$ phases (Figure 4.3). Alternatively, a similar reaction was performed between samarium diiodide and DSP as the selenium precursor; however, an amorphous material was observed and this route for samarium selenide was not probed further. Therefore, it can be concluded that reducing samarium is challenging, and even under excess sulfur and reducing conditions, we are limited to the mixed valent Sm$_3$S$_4$ phase.
Figure 4.3. PXRD comparison of samarium sulfide compositions via solid state routes. Sm$_2$O$_2$S forms in sulfur-poor conditions (bottom, SEI-127-A) and Sm$_3$S$_4$ forms in sulfur-rich conditions (top, SEI-143-A). Under intermediate conditions (middle, SEI-129-A), a mixture of Sm$_2$O$_2$S (red asterisk) and Sm$_3$S$_4$ (blue circles) are observed.
Annealing the prepared oxysulfide phase under flowing hydrogen sulfide proves to be a challenging route for SmS (Figure 4.4). Under specific conditions at 700°C for 3 hours, it is observed that some Sm$_2$O$_2$S converts to SmS, potentially indicating the need for either a higher annealing (i.e. decomposition) temperature or a longer reaction time. However, an increase in both time and temperature (1000°C for 5 hours) results in the formation of pure Sm$_3$S$_4$, while solely an increase in temperature to 1000°C for 3 hours also resulted in the formation of pure phase Sm$_3$S$_4$. Decreasing the annealing temperature to 600°C for 5 hours, also produces some SmS; however, the material is not as crystalline as that material obtained at 700°C for 3 hours. From these results, it can be observed that Sm$^{2+}$ is easily oxidized to form Sm$^{3+}$ or mixed valent compositions at high temperatures, further supporting literature reports regarding the instability and sensitivity of divalent samarium compounds.

Previously, Schaak has demonstrated that iron selenide and iron sulfide materials could be tuned using trioctylphosphine (TOP) to extract selenium or sulfur, respectively.$^{38}$ For instance, this method was employed for iron selenide via the reaction

$$\text{Fe}_3\text{Se}_4 + \text{TOP} \rightarrow \text{tet-FeSe} + \text{TOP-Se}$$

We adapted this approach as a potential route for composition control in samarium chalcogenide materials. In this reaction, a prepared sample of Sm$_3$S$_4$ was dispersed in trioctylphosphine and heated at 200°C for 30 minutes with the goal of forming SmS and TOP-S; however, the resulting diffraction pattern did not reflect any changes. Although this reaction has proved to be effective for several transition metal chalcogenide systems, the appropriate temperature at which the reaction occurs varies. For example, sulfur extraction from FeS$_2$ to give FeS requires a reaction
temperature of 255°C and selenium extraction from Fe$_3$Se$_4$ to give FeSe occurs at 180°C. Temperature requirements for rare earth chalcogenide materials may be quite different.

Figure 4.4. PXRD comparison of Sm$_2$O$_2$S annealing conditions. (A) At 700°C for 3 hours, Sm$_2$O$_2$S is partially converted to SmS in SEI-128-A (noted in blue), whereas (B) 1000°C for 5 hours results in complete conversion to Sm$_3$S$_4$ in SEI-230-A.
4.3.2 Synthetic Approaches for Samarium Sulfide Nanomaterials

The synthesis of samarium sulfide nanomaterials was investigated via the hot injection method. As with other synthetic approaches, precursor selection is critical in establishing phase control, and a divalent samarium precursor would be ideal so as to avoid redox chemistry for the formation of SmX. However, the commercially available samarium diiodide is not soluble in the high boiling point capping ligands or solvents traditionally used in the hot injection method. As a result, samarium acetate (Sm$^{3+}$) was utilized, thereby requiring a reducing environment to favor Sm$^{2+}$. Various sulfur precursors and reactions conditions were investigated and are summarized in Table 4.1.

Table 4.1. Reaction conditions for samarium sulfide via the hot injection method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S-precursor</th>
<th>Capping ligand/solvent</th>
<th>Reaction Time</th>
<th>Color</th>
<th>PXRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>142</td>
<td><img src="image" alt="DTP" /></td>
<td>OLA</td>
<td>1 hr</td>
<td>White</td>
<td>Amorphous</td>
</tr>
<tr>
<td>144</td>
<td><img src="image" alt="Thiourea" /></td>
<td>OLA</td>
<td>1 hr</td>
<td>White</td>
<td>SmS / Sm$_2$O$_3$</td>
</tr>
<tr>
<td>152</td>
<td><img src="image" alt="Substituted thiourea" /></td>
<td>OLA</td>
<td>1 hr</td>
<td>White</td>
<td>Amorphous</td>
</tr>
<tr>
<td>188</td>
<td>'BuSS'Bu</td>
<td>OLA</td>
<td>1 hr</td>
<td>Yellow</td>
<td>SmS / Sm$_3$S$_4$</td>
</tr>
<tr>
<td>189</td>
<td>'BuSS'Bu</td>
<td>OLA</td>
<td>&gt;1 hr</td>
<td>Yellow</td>
<td>SmS / Sm$_3$S$_4$</td>
</tr>
<tr>
<td>191</td>
<td>'BuSS'Bu</td>
<td>OLA/HDA</td>
<td>&gt;1 hr</td>
<td>Yellow</td>
<td>SmS / Sm$_3$S$_4$</td>
</tr>
<tr>
<td>192</td>
<td>'BuSS'Bu</td>
<td>OLA/ODE</td>
<td>&gt;1 hr</td>
<td>Yellow</td>
<td>SmS / Sm$_3$S$_4$</td>
</tr>
</tbody>
</table>
To provide a reducing environment, oleylamine was employed in all syntheses. The DTP precursor has also shown to be slightly reducing in other systems; however, its use for samarium sulfide afforded an amorphous material. Turning to the literature, thiourea and substituted thiourea compounds have been reported as sulfur precursors for the synthesis of PbS nanomaterials, which also have the NaCl cubic structure type. By modifying the organic substituents to form substituted thiourea compounds, it is possible to ‘tune’ the reaction kinetics to control nanoparticle size. Although we are not yet aiming to control size or shape of samarium chalcogenide nanomaterials, we may be able to take advantage of the relative reactivity of chalcogen precursors for the synthesis of samarium chalcogenide nanoparticles. Employing thiourea in the hot injection method with samarium acetate resulted in a poorly crystalline material that most closely indexed to a mixture of SmS and Sm$_2$O$_3$. Therefore, bulky alkyl substituents on a disubstituted thiourea compound, such as that shown in Table 4.1, is expected to decrease the rate of reaction and potentially nucleate more SmS. However, an amorphous material was obtained. Based on these observations, it is possible that SmS is the kinetically favored product – although with poor crystallinity – and a more reactive sulfur precursor may help isolate divalent samarium. As a result, we turned our attention to the diorganyl dichalcogenides (R-E-E-R, where E = S, Se or Te) as potential chalcogen precursors. The relative reactivity of diorganyl dichalcogenides have been reported (Figure 4.5) for a wide range of metal chalcogenide nanocrystals, including CdS, CdSe, and ZnSe. These dichalcogenides possess weak E-E bonds and the organic substituents can be tuned to affect the reactivity. Of these, the di-$t$-butyl disulfide compound of moderate reactivity was investigated as a potential sulfur precursor for samarium sulfide. A pale, yellow powder was isolated and PXRD analysis showed a poorly crystalline sample of Sm$_3$S$_4$ and SmS (Figure 4.6).
Crystallinity did not improve with reaction time or with alternative capping ligands, such as hexadecylamine, or noncoordinating solvents, like octadecene. More reactive diorganyl disulfides are not commercially available for purchase, thereby limiting the scope of our investigation.

Figure 4.5. Relative reactivity of diorganyl dichalcogenides. Reprinted with permission from Guo, Y. et.al. ACS Nano. 2013, 7, 3616. Copyright 2013 American Chemical Society.
Figure 4.6. PXRD of samarium sulfide using a diorganyl disulfide precursor. The poorly crystalline sample, SEI-191-A, may be SmS (red), Sm$_3$S$_4$ (blue), or a mixture of the two.

Alternatively, efforts to employ a solution of divalent samarium via the hot injection method were made. Although samarium diiodide is not soluble in oleylamine, it is known to be soluble in tetrahydrofuran (THF). The boiling point of THF at 150°C may limit the temperatures needed via solid state approaches and other solvents were investigated. Tetraglyme, a highly polar solvent, has a boiling point of 275°C; however, SmI$_2$ was found to be only partially soluble in tetraglyme and an amorphous material was obtained via these efforts. Furthermore, the oxygen presence in THF and tetraglyme are undesirable due to samarium’s oxophilic nature. Instead, SmI$_2$ was found to be soluble in acetonitrile (bp=180°C) so a solution of samarium diiodide in acetonitrile was prepared and added to a capping ligand solution of oleylamine and octadecene.
Oleylamine was employed as a capping ligand to protect the surface of as-synthesized nanomaterials from oxidation and octadecene was employed as a high boiling point solvent. Here, the highly reactive bis(trimethylsilyl)sulfide compound was employed as the sulfur precursor since a reactive precursor may influence particle formation from aqueous Sm$^{2+}$ to stabilize and form SmS. At low temperatures (150°C), the reaction resulted in a highly crystalline material (Figure 4.7A). Although this reaction is reproducible, efforts to identify this material have not been successful. SEM reveals large micron sized plates or sheets as well as cubic nanomaterials. EDX analysis of six regions reveal the presence of samarium (39%), iodine (9%), sulfur (1%), oxygen (30%), and carbon (20%) in both morphologies (Figure 4.8). The diffraction pattern does not index to any known phase including any combination of elements identified by EDX. It is possible that some complex has formed, but it is unlikely that any complex formed contains an Sm-S bond to serve as a single source precursor given the small amount of sulfur present when compared to samarium. Also, very little material is produced in this reaction and thus cannot be probed further.

Performing a similar reaction at higher temperatures (300°C) produces a mixture of SmS and Sm$_2$O$_2$S (Figure 4.7B).
Figure 4.7. PXRD comparison from a divalent samarium precursor. (A) Reaction of SmI$_2$ and (TMS)$_2$S at 150°C and (B) at 300°C, SmS (red) and Sm$_2$O$_2$S (blue).
4.3.3 Synthetic Approaches for Samarium Selenide Nanomaterials

The synthesis of samarium selenide nanomaterials was also investigated via the hot injection method, similar to the approaches discussed for samarium sulfide. In the reaction of samarium acetate and a selenium precursor – either DSP or diphenyldiselenide (PhSeSePh) – a dark purple powder is isolated. Powder X-ray diffraction analysis of the purple powder (Figure 4.9) shows a poorly crystalline material that cannot be clearly identified but the peak at 2θ = 31.958° most closely matches the (310) peak of Sm$_3$Se$_4$ or Sm$_2$Se$_3$. The phase cannot be determined with certainty because of the poor crystallinity, which was not improved with reaction time over the range of 30 minutes to 17 hours or with modifications to the capping ligand solution. SEM consistently reveals a spiked material with nanowire formations approximately 10 nm in diameter and 200-250 nm in length. The nanowires appear to be crystalline based on the TEM images obtained and match the diffraction pattern since the (hk0) reflections for Sm$_3$Se$_4$ are observed for preferred orientation. EDX analysis of the nanowires indicate the presence of samarium and selenium in a ratio of an average 4.4 to 1. Although this is against what we observe via diffraction techniques, there may be amorphous samarium present within the sample in
addition to Sm$_x$Se$_y$. Further analysis of individual components of the spiked material would need to be performed to determine where any amorphous samarium may be concentrated. It is also important to note that the samarium valency in Sm$_3$Se$_4$ and Sm$_2$Se$_3$ differ in that Sm$_3$Se$_4$ contains some divalent samarium whereas Sm$_2$Se$_3$ is purely trivalent. X-ray photoelectron spectroscopy techniques could provide insight into the samarium valency to determine the phase present.

Based on the assumption that the purple powder obtained contains Sm$_x$Se$_y$, borane tert-butyl amine (TBAB), was employed as a co-reductant with oleylamine in the hot injection method. TBAB has been used in the literature for the synthesis of metal nanoparticles, such as Pd$^{82}$ and Ni-Pd alloyed nanoparticles.$^{83}$ Both materials were formed from the reduction of Pd$^{2+}$ and Ni$^{2+}$ precursors via the hot injection method. These reports also show that TBAB can also influence the formation of monodisperse nanoparticles with size control. By employing TBAB in our syntheses, we may be able to further reduce samarium for the formation of SmS. However, in this approach, a purple material is still obtained and PXRD analysis of this poorly crystalline material cannot be clearly identified. However, it is noted that the peak at 2$\theta$ = 29.641° most closely matches the (200) peak for SmSe and the peak at 2$\theta$ = 31.801° most closely matches the (310) peak for Sm$_3$Se$_4$ or Sm$_2$Se$_3$ (Figure 4.10). It is possible that TBAB is able to partially reduce samarium to form some SmSe when compared to the synthetic routes discussed previously in the absence of TBAB (Figure 4.9), although the diffraction pattern is quite broad and therefore cannot be matched well to either samarium selenide composition to make any conclusions.
Figure 4.9. Characterization of purple samarium selenide material. (A) PXRD analysis most closely matches Sm$_3$Se$_4$, (B) SEM showing spiked material and (C) TEM of the crystalline wires (inset).
Figure 4.10. PXRD of samarium selenide material. The representative sample, SEI-213-A, shows Sm$_3$Se$_4$ (red) and SmSe (blue).

4.4 Conclusion

Ultimately, we are interested in the synthesis of samarium chalcogenide nanomaterials, particularly SmX. However, like many other metal chalcogenide systems, the samarium chalcogenides exhibit multiple stable phases, and appropriate precursor selection may afford the opportunity to establish phase control for these systems. Solid state routes serve as a means to test the thermal decomposition of precursors, and this work demonstrates the ability to synthesize Sm$_3$S$_4$ from samarium diiodide (Sm$^{2+}$) in the presence of excess sulfur and reducing conditions.
Although some SmS has been observed from annealing Sm$_2$O$_2$S under flowing H$_2$S, the specific conditions favoring SmS have proven to be challenging to fine-tune. Although pure phase SmX has not been isolated via solid state approaches, the chemistry of our precursors was also investigated via solution phase routes for the synthesis of nanomaterials. Despite studying various samarium precursors, chalcogen precursors, and other reaction conditions (capping ligand/reducing agents), poorly crystalline mixtures of what can be attributed to be SmX and Sm$_x$X$_y$, where X = S or Se, have been obtained. Overall, the oxophillic nature of divalent samarium is demonstrated, in both the solid state and the nanoscale approaches. We predict that an even stronger reducing environment and/or more reactive precursors may afford the opportunity to synthesize pure phase SmX. However, the stability of Sm$^{3+}$ is of interest in samarium doped europium selenide systems, which is discussed in Chapter 5.
CHAPTER 5. SAMARIUM-DOPED EUROPium CHALCOGENIDE NANOMATERIALS

5.1 Introduction

At room temperature and zero pressure, the samarium chalcogenides, SmS and SmSe, are semiconductors of the NaCl cubic structure type containing divalent samarium. However, under modest pressure, divalent samarium converts to trivalent samarium via an isostructural transition and a contraction of the unit cell.\(^\text{69}\) Alloys of Sm\(_{1-x}\)Se\(_x\) have been modeled and can provide insight into the transition mechanism from discontinuous SmS to continuous SmSe. In fact, the solid solution of bulk Sm\(_{1-x}\)Se\(_x\) (0 ≤ \(x\) ≤ 1) obeys Vegard’s law such that the corresponding lattice constants vary linearly with concentration. In the samarium chalcogenide solid solution, this can also be reflected in evaluating the volume collapse to determine the critical pressure at which the transition occurs, which is calculated to change linearly with composition. (Figure 5.1).

Alternatively, europium chalcogenides can serve as a model for studying other lanthanide chalcogenide systems. The europium chalcogenides belong to a unique class of semiconductors that exhibit highly coupled electronic and magnetic properties. For example, EuS is a ferromagnetic semiconductor with a band gap (\(E_g\)) of 1.65eV and a ferromagnetic ordering temperature of 16K, and EuSe is an antiferromagnetic semiconductor (\(T_N=4.6\)K, \(E_g=1.80\)eV).\(^\text{84}\) These materials have been studied extensively in recent years, particularly in efforts to establish size and shape control for fine-tuning the properties of interest.
Figure 5.1. Volume and transition pressures for SmS$_{1-x}$Se$_x$, $0 \leq x \leq 1$. Based on the calculated volume collapse corresponding to each concentration (inset), the transition pressure was extrapolated and is observed to vary linearly with concentration ($x$). Reproduced with permission from Elsevier.\textsuperscript{70}

One route to study or fine-tune the electronic properties of semiconductors is via doping, or substituting one atom for another atom of similar size and valency. Of the lanthanides, europium is a redox active metal in which the divalent state is stable for EuX and has a large cell constant, whereas gadolinium is non-redox active due to the stability of its half-filled $f$-orbital. As a result, gadolinium sulfide can be represented as Gd$^{3+}$(e$^{-}$)S (Figure 5.2). Since the highly coupled magnetic and electronic properties of europium chalcogenides can be enhanced via the promotion of electrons into its conduction band, solid solutions of bulk EuSe-GdSe have been studied where gadolinium proves to be an electron donor.\textsuperscript{85} As such, charge balance in Eu$_{1-x}$(Gd$^{3+}$ + e$^{-}$)$_x$Se is maintained by the delocalization of an electron into the conduction band, and an in $T_c$ is reported.
for low doping levels of gadolinium. Therefore, composition control of europium chalcogenide systems with electron donors, like Gd$^{3+}$, are of interest.

![Figure 5.2. Cell constants of LnS across the lanthanide series. Image reproduced with permission from Elsevier.]

Because of the relative stability of trivalent samarium on the nanoscale (as discussed in Chapter 4), Sm$^{3+}$ may also act as an electron donor in doped europium chalcogenide systems. Solid solutions of bulk Eu$_{1-x}$Sm$_x$Se have been reported and show a decrease in cell constant at low doping levels (Figure 5.3), indicating the presence of the smaller Sm$^{3+}$ cation as opposed to the Sm$^{2+}$ cation. Because bulk SmSe and EuSe have similar cell constants of about 6.2Å, establishing control over composition in the solid solution can allow for band gap engineering. Particularly, nanomaterials of Eu$_{1-x}$Sm$_x$Se may afford the opportunity to further fine-tune smaller changes in the lattice parameters and the resulting effects on the properties of interest, specifically at lower doping levels. Herein, we report the synthesis of Eu$_{1-x}$Sm$_x$Se nanomaterials where $0 \leq x \leq 0.10$. This work mirrors another project that is specifically studying the effects of low doping levels on the lattice constant in bulk Eu$_{1-x}$Sm$_x$Se.
5.2 Experimental Section

5.2.1. General Information

Europium (III) chloride hexahydrate, samarium (III) chloride hexahydrate, sodium oleate, oleylamine (OLA, 70%), hexadecylamine (HDA, 98%), and 1-octadecene (ODE, 90%) were purchased from Sigma-Aldrich. Hexanes and ethanol were obtained from Fisher Scientific. Diethylammonium diphenyldiselenophosphinate (DSP) was synthesized as previously reported (Section 2.2.1). The synthesis of samarium oleate and europium oleate were adapted from the literature. In brief, europium (III) chloride hexahydrate or samarium (III) chloride and three-equivalents of sodium oleate were dissolved in a mixture of 1:1:2 deionized water:ethanol:hexanes and refluxed 4 hours. The organic phase was separated and washed three times with deionized water. Removal of the solvent under vacuum afforded Eu(oleate)₃ or Sm(oleate)₃, respectively. X-ray powder diffraction patterns were obtained using a Rigaku Ultima IV X-Ray powder diffractometer with Cu Kα radiation and a DTex detector. SEM images were taken with a Zeiss
SUPRA 55-VP Scanning Electron Microscope at an acceleration voltage of 9-20 kV with an in-lens detector. High resolution TEM was performed with a JEOL JEM 2100F Field Emission Gun Transmission Electron Microscope at 200 kV at the University of Maryland Nanoscale Imaging Spectroscopy and Imaging Laboratory.

5.2.2 Nanoparticle Syntheses

**EuSe nanoparticles.** A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. Europium oleate (0.3990 g, 0.4005 mmol), HDA (2.3468 g) and ODE (7.5 mL) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and allowed to reflux at 330°C. Meanwhile, the Se-precursor solution was prepared in the glove box by dissolving DSP (0.0412 g, 0.09874 mmol) in OLA (5.0 mL). The Se-solution was injected into the hot capping ligand solution. The reaction mixture heated 60 minutes and then slowly cooled to room temperature. The resulting purple product was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD for a representative sample SEI-216-A was obtained to show pure phase EuSe (PDF #01-074-5111): 24.674°, 3.6053Å; 28.579°, 3.1208Å; 40.961°, 2.2015Å; 48.482°, 1.8761Å; 50.820°, 1.7952Å; 59.442°, 1.5537Å; 65.404°, 1.4258Å; 67.362°, 1.3890Å; 74.860°, 1.2674Å.

**Eu<sub>1-x</sub>Sm<sub>x</sub>Se nanoparticles, 0 ≤ x ≤ 0.10.** A three-neck round-bottom flask was equipped with a condenser, thermocouple adapter, and stopper. Appropriate amounts of europium oleate and samarium oleate (total metal amount = 0.4 mmol), HDA (2.3460 g) and ODE (7.5 mL) were added to the round bottom flask and degassed at 120°C for 1 hour. The apparatus was purged with nitrogen and allowed to reflux at 330°C. Meanwhile, the Se-precursor solution was prepared in the glove box by dissolving DSP (0.0419 g, 0.1004 mmol) in OLA (5.0 mL). The Se-solution was
injected into the hot capping ligand solution. The reaction mixture heated 60 minutes and then slowly cooled to room temperature. The resulting purple product was isolated via centrifugation and washed with a mixture of hexanes and ethanol several times. PXRD of a representative sample, SEI-218-A (Eu$_{0.90}$Sm$_{0.10}$Se), was obtained to show EuSe (PDF #01-074-5111) or SmSe (PDF#01-074-1342): 24.696°, 3.6020Å; 28.678°, 3.1103Å; 41.040°, 2.1975Å; 48.562°, 1.8732Å; 50.918°, 1.7919Å; 59.543°, 1.5513Å; 65.607°, 1.4218Å; 67.421°, 1.3879Å; 74.980°, 1.2656Å.

5.3 Results and Discussion

Europium selenide nanomaterials have been synthesized via the hot injection method using europium oleate (Eu$^{3+}$) and DSP, resulting in the characteristic brick-red color. Although a trivalent europium precursor is employed, DSP and oleylamine provide reducing conditions for divalent europium. PXRD shows pure phase EuSe (Figure 5.4), and the sharp, narrow peaks indicate a high level of crystallinity.
Figure 5.4. PXRD of EuSe.

Since we can demonstrate the synthesis of EuSe with our precursors, the synthesis of samarium-doped europium selenide nanomaterials has been tested at low doping levels, where $0.05 \leq x \leq 0.10$. This range was targeted based on the reports of a decrease in the cell constant in the solid solution of bulk Eu$_{1-x}$Sm$_x$Se. Here, samarium oleate and europium oleate are reacted in appropriate amounts with DSP via the hot injection. Like europium oleate, samarium oleate affords Sm$^{3+}$. Although Eu$^{3+}$ can be reduced in the reaction conditions tested, we acknowledge that samarium chemistry is quite different and Sm$^{3+}$ is stable. As a result, we expect that samarium will remain trivalent and act as an electron donor in these doped systems. Diffraction analysis of the resulting material indicates what might appear to be pure phase EuSe (Figure 5.5). However, because EuSe and SmSe have similar lattice constants, their diffraction patterns are nearly identical.
Electron microscopy of Eu$_{0.90}$Sm$_{0.10}$Se shows nanocubes approximately 100nm across. Line scan analysis of the nanocubes reveals the presence of europium, samarium, and selenium across the nanoparticle, as expected (Figure 5.6).
Figure 5.6. Characterization of Eu$_{0.90}$Sm$_{0.10}$Se nanomaterials. TEM image and line scan analysis indicating the presence of selenium (red), europium (blue), and samarium (green).

At this point, it is unknown whether samarium exists on the surface of the nanomaterials or has passivated the surface to replace europium sites within the crystal structure. A closer look at the diffraction peaks can provide insight into this, where a shift to a higher 2θ would be indicative of a smaller cell constant and the incorporation of the smaller Sm$^{3+}$ cation. In fact, an analysis of our materials does reveal a shift to higher 2θ for the synthesized Eu$_{0.90}$Sm$_{0.10}$Se when compared to pure phase EuSe (Figure 5.7).
Figure 5.7. Shift in diffraction peaks for $\text{Eu}_{1-x}\text{Sm}_x\text{Se}$. A shift towards higher 2θ is observed from EuSe (black) to Eu$_{0.90}$Sm$_{0.10}$Se (blue).
In studying the effects of other doping levels, Eu_{0.95}Sm_{0.05}Se appeared to more closely match the synthesized pure phase EuSe. For instance, the (200) peaks of the doped and undoped materials were identically placed at θ=28.579°. It is possible that doping levels this low may be challenging to characterize for any evidence of samarium incorporation, especially via PXRD. It is also true that the actual dopant concentration may be less than the target dopant concentration. Further analysis using ICP-MS can better determine the amount of europium and samarium within the synthesized materials. At a slightly higher doping level, Eu_{0.92}Sm_{0.08}Se revealed a small shift to a larger 2θ in the diffraction peaks (Table 5.1).

Table 5.1. Diffraction peaks for Eu_{1-x}Sm_xSe, where x = 0, 0.08, and 0.10.

<table>
<thead>
<tr>
<th></th>
<th>EuSe</th>
<th>Eu_{0.92}Sm_{0.08}Se</th>
<th>Eu_{0.90}Sm_{0.10}Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>(200)</td>
<td>28.579°</td>
<td>28.581°</td>
<td>28.678°</td>
</tr>
<tr>
<td>(220)</td>
<td>40.961°</td>
<td>40.979°</td>
<td>41.040°</td>
</tr>
<tr>
<td>(222)</td>
<td>50.820°</td>
<td>50.839°</td>
<td>50.918°</td>
</tr>
<tr>
<td>(420)</td>
<td>67.362°</td>
<td>67.400°</td>
<td>67.421°</td>
</tr>
<tr>
<td>(422)</td>
<td>74.860°</td>
<td>74.881°</td>
<td>74.980°</td>
</tr>
</tbody>
</table>

On the other hand, the diffraction peaks for Eu_{0.88}Sm_{0.12}Se consistently showed a shift to smaller 2θ, indicating a larger cell constant and possibly the incorporation of Sm^{2+} as opposed to Sm^{3+}. However, these results can help to establish a range of dopant concentrations of 0.05 < x < 0.12 to be further studied on the nanoscale.

5.4 Conclusion

Samarium doped europium selenide nanomaterials may afford the opportunity to fine-tune the electronic properties of the resulting material. In particular, samarium may act as an electron donor, thereby promoting electrons into the conduction band, such that Eu_{1-x}(Sm^{3+} + e^-)_xSe. To probe samarium’s ability to serve as an electron donor, Eu_{1-x}Sm_xSe nanomaterials have been
synthesized at low doping levels. Eu$_{0.90}$Sm$_{0.10}$Se shows the incorporation of samarium within the nanomaterial via TEM line scan. PXRD analysis shows a shift in the diffraction peaks to a higher 2θ indicating a smaller cell constant, which translates to the incorporation of the smaller Sm$^{3+}$ cation as opposed to Sm$^{2+}$. PXRD of Eu$_{0.92}$Sm$_{0.08}$Se also indicates a decrease in the cell constant. On the other hand, no change is observed in Eu$_{0.95}$Sm$_{0.05}$Se and higher doping levels for Eu$_{0.88}$Sm$_{0.12}$Se results in a larger cell constant, which may indicate the incorporation of Sm$^{2+}$. As a result, it can be observed that at low doping levels where 0.05 < \( x \) < 0.12, trivalent samarium exists and can thereby act as an electron donor in these doped systems. This mirrors work done in the bulk EuSe-SmSe solid solutions and provides insight into means for enhancing the electronic properties of EuSe.
6.1 Introduction

Laboratory work is a significant component of most chemistry courses by enabling students to experience chemistry through scientific discovery. Several pedagogical approaches exist to teach chemistry in a laboratory environment. In General Chemistry, confirmation experiments have traditionally been the most widely-used lab type, providing step-by-step procedures for students to follow and collect data in a ‘cookbook’ format.\textsuperscript{88,89} However, confirmation labs have been criticized because student initiative, hypothesis development, understanding of the materials or concepts, and the observation of negative results are limited.\textsuperscript{90} As a result, there has been a large movement towards inquiry-based learning in the laboratory. Since the earliest reports of inquiry-based learning experiments in the 1970s,\textsuperscript{88} the term ‘inquiry’ has taken on several definitions and can be presented in many ways.\textsuperscript{89,91,92} More recently, a rubric was designed which classifies the level of inquiry-based laboratory activities and experiments.\textsuperscript{93} Level 0 are the confirmation labs traditionally utilized. Level ½, or structured inquiry, experiments provide the problem, procedures, and analysis steps to answer a specific question. Level 1 guided-inquiry labs can either (1) provide a question prompting students to design an experiment with some guidance or (2) students may be provided a procedure as a means to learn or understand concepts before they are formally introduced by the instructor.\textsuperscript{94} In both Level 0 and Level ½ experiments the expected outcomes are known to the instructor, but unknown to the students, implementing an inductive approach to chemistry problems and allowing students to observe both positive and negative results.\textsuperscript{95}

Alternatively, open (Level 2) and authentic inquiry (Level 3) labs are less structured experiments that require less direct guidance from the instructor. Open inquiry experiments
provide a problem and background in which students are prompted to design a procedure, perform data analysis, and draw conclusions.\textsuperscript{93,94} Authentic inquiry experiments require students to propose a question, devise their own experiment to investigate that problem, and predict and analyze their results, mimicking scientific research\textsuperscript{93} which can be challenging for both instructor and student.\textsuperscript{96} Overall, implementation of inquiry-based experiments requires careful consideration from the instructor.\textsuperscript{97}

The benefits of inquiry-based experiments in chemistry courses have been documented in the literature,\textsuperscript{88,95,98–105} and, as a result, the movement towards inquiry-based labs has also been observed in other scientific fields\textsuperscript{93,106} and high school chemistry courses.\textsuperscript{99,107} In fact, the College Board recently published an inquiry-based laboratory manual for use in AP Chemistry Courses.\textsuperscript{108} However, these reports are less robust as they are solely conducted over the course of one or two semesters and are often narrowly focused. For example, one study reports students’ positive feedback towards both guided-inquiry and open-inquiry labs, but the data is only based on the responses from one semester of a general chemistry course and primarily focuses on educating students in identifying each format.\textsuperscript{101}

As a result, a five-year study has been conducted at Georgetown University to evaluate student perceptions of a guided and authentic inquiry-based General Chemistry Laboratory for Majors course. The central goals of this study are to (1) evaluate student perceptions and attitudes towards both guided and authentic inquiry-based laboratory experiments, and (2) to determine whether guided inquiry lab experiments are a useful tool in preparing students for the authentic inquiry freelance lab projects.
6.2 Experimental Section

6.2.1 Methodology

Study participants were students enrolled in a General Chemistry Laboratory for Chemistry and Biochemistry Majors course at Georgetown University. The survey used in this study was distributed at the end of the Spring General Chemistry II course each year from 2013-2017. A total of 115 students participated in the survey over five years (Table 6.1).

<table>
<thead>
<tr>
<th>Year</th>
<th>Female Number</th>
<th>Female Percentage</th>
<th>Male Number</th>
<th>Male Percentage</th>
<th>No response</th>
<th>Total number of students</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>13</td>
<td>44.8%</td>
<td>16</td>
<td>55.2%</td>
<td>0</td>
<td>29</td>
</tr>
<tr>
<td>2014</td>
<td>11</td>
<td>42.3%</td>
<td>13</td>
<td>50.0%</td>
<td>2</td>
<td>26</td>
</tr>
<tr>
<td>2015</td>
<td>13</td>
<td>54.2%</td>
<td>11</td>
<td>45.8%</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>2016</td>
<td>11</td>
<td>45.8%</td>
<td>13</td>
<td>54.2%</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>2017</td>
<td>7</td>
<td>58.3%</td>
<td>4</td>
<td>33.3%</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>TOTAL</td>
<td>55</td>
<td>49.1%</td>
<td>57</td>
<td>47.7%</td>
<td>3</td>
<td>115</td>
</tr>
</tbody>
</table>

The General Chemistry lab for Majors course meets three times per week: twice a week for a 50-minute recitation, and once a week for 3-hour lab following the recitation. The recitations and lab are led by a Chemistry Graduate Student Teaching Assistant (TA). The course TAs are also responsible for student assessment and must provide feedback on lab assignments (proposed procedures, pre-lab questions, post-lab questions/reports). The TAs are trained on the guidelines of inquiry-based instruction in weekly meetings with the laboratory instructor.

The lab experiments performed in the course include a variety of formats – confirmation (1-2 each semester), guided-inquiry (5-6 each semester), and authentic inquiry (1 each semester) – followed in a one-week time frame (Fall semester) or two-week time frame (Spring semester) (Figure 6.1).
Figure 6.1. Schematic representation of one-week versus two-week lab formats.

The guided-inquiry experiments are adapted from the textbook “Laboratory Inquiry in Chemistry”, \(^{109}\) and are classified as Level \(\frac{1}{2}\) (structured inquiry) or Level 1 (guided inquiry). \(^{93}\) The authentic inquiry experiment is a semester-long freelance lab project in which students work in pairs to design a unique experiment based on the concepts and techniques learned throughout the semester. The process includes submissions for a topic proposal, proposed procedure, two weeks for experiment completion, followed by data analysis and data communication (lab report in the Fall term and a poster presentation in the Spring term).

6.2.2 Instrument

A semantic differential survey\(^{110}\) was conducted annually from 2013 to 2017 in the last week of spring semester classes. Statements were presented similar to those of Birnie-Abraham-Renner (BAR) Quick Attitude Differential\(^{111}\) and provided students with a five-point Likert scale for a series of 16 to 19 statements regarding the guided-inquiry laboratory format. Students circled 1 or 2 if they strongly agreed or moderately agreed with the statement on the left, 3 if they did not
agree with either statement, and 4 or 5 if they moderately agreed or strongly agreed with the statement on the right. When first introduced to the guided-inquiry format, ample time is spent explaining the definition of and expectations associated with the guided-inquiry and authentic-inquiry experiments. Reliability was ensured by employing 1-2 confirmation labs each semester. The survey also requested biographical information, such as gender, expected grade, intention to continue as a Chemistry/Biochemistry major, and previous experience with guided-inquiry labs. The original survey format utilized in 2013-2015 was adjusted in 2016 and 2017 to include additional statements and a “comments/suggestions” section was added to prompt student feedback. The construct validity of the BAR Quick Attitude Differential was carried using factor analysis.

6.3 Results and Discussion

The statistical analysis of students’ responses over the course of five years are shown in Tables 6.2 and 6.3. In short, the leftmost column indicates the percentage (%) of the total students that reported an overall agreement with the statement on the left - those that either circled 1 (strongly agree) or 2 (moderately agree). The column on the right shows the percentage (%) of the total students that agreed with the statement on the right - those that either circled 4 (strongly agree) and 5 (moderately agree). Note that the ‘strongly agree’ and ‘moderately agree’ responses were combined because the level of agreement with a given statement was not studied but instead an overall agreement with one statement versus an alternative statement. The results are reported as such. The ‘no opinion’ column shows the percentage (%) of the total students that did not agree with either statement.
In regards to the guided-inquiry lab workload (Table 6.2), most students indicate that guided inquiry lab activities take more time (82 ± 14%) and effort (55 ± 20%) to complete. Furthermore, students also agree that the corresponding lab reports required more effort (87 ± 7%) and time (91 ± 5%) when compared to confirmation lab reports. On average, 70 ± 4% of students thought that the guided inquiry labs require a lot of thinking and analyzing. These results can be attributed to the additional steps involved in the guided-inquiry format, including the procedural development process in addition to the requirement that students work with a different lab partner each week.

Despite the consensus that guided-inquiry labs require a lot of time and effort, students agree that this format has a multitude of benefits (Table 6.3) including the development of critical thinking and problem solving skills (71 ± 17%), increased communication skills (40 ± 17%), an understanding of the concepts in greater depth (70 ± 11%), greater confidence in chemistry (57 ± 15%) and a better learning of the scientific process (67 ± 20%). These benefits are also reflected in student performance in the class as well as student ability to create and complete an authentic inquiry lab. Although the literature argues that students are poor predictors of learning outcomes, such as critical thinking, several emerging themes that students, teaching assistants, and employers all correlate with the term ‘critical thinking’ have been reported. Students participating in our study commented that the guided-inquiry lab format “help[ed] increase understanding”, “greatly improved…reasoning skills”, and “improved…capacity to evaluate scientific experiments before performing them”. Overall, a moderate majority of the students report that they prefer the guided inquiry format (54 ± 20%) as opposed to traditional formats and more than half (63 ± 26%)
recommended using the guided inquiry based lab format in the General Chemistry Lab for Majors course.

Table 6.2. Distribution of semantic differential survey results about guided-inquiry lab activity workload.a

<table>
<thead>
<tr>
<th>Statement Number</th>
<th>Left Statement</th>
<th>Agreement w/ left statement</th>
<th>No opinion</th>
<th>Agreement w/ right statement</th>
<th>Right Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Guided inquiry labs are easy to do.</td>
<td>18.1% ± 4.7%</td>
<td>42.7% ± 7.4%</td>
<td>39.2% ± 9.4%</td>
<td>Guided inquiry labs are difficult to do.</td>
</tr>
<tr>
<td>2</td>
<td>Guided inquiry labs take a short time to complete.</td>
<td>6.4% ± 5.6%</td>
<td>12.1% ± 10.6%</td>
<td>81.6% ± 14.2%</td>
<td>Guided inquiry labs take a long time to complete.</td>
</tr>
<tr>
<td>3</td>
<td>Guided inquiry lab reports are easy to do.</td>
<td>9.5% ± 8.2%</td>
<td>35.6% ± 15.9%</td>
<td>54.9% ± 20.4%</td>
<td>Guided inquiry lab reports are difficult to do.</td>
</tr>
<tr>
<td>4</td>
<td>It takes a small amount of time to complete the guided inquiry lab reports.</td>
<td>0.8% ± 1.8%</td>
<td>7.9% ± 5.6%</td>
<td>91.3% ± 5.2%</td>
<td>It takes a large amount of time to complete the guided inquiry lab reports.</td>
</tr>
<tr>
<td>5</td>
<td>It takes a small amount of effort to complete guided inquiry lab reports.</td>
<td>3.0% ± 4.1%</td>
<td>10.2% ± 5.0%</td>
<td>86.8% ± 6.7%</td>
<td>It takes a large amount of effort to complete guided inquiry lab reports.</td>
</tr>
<tr>
<td>6</td>
<td>I do not have to do a lot of thinking and analyzing for doing guided inquiry lab reports.</td>
<td>12.8% ± 3.9%</td>
<td>17.0% ± 4.9%</td>
<td>70.2% ± 4.1%</td>
<td>I have to do a lot of thinking and analyzing for doing guided inquiry lab reports.</td>
</tr>
<tr>
<td>7</td>
<td>I like to come up with my own procedure for doing the labs.</td>
<td>34.3% ± 9.9%</td>
<td>32.9% ± 13.8%</td>
<td>32.8% ± 14.8%</td>
<td>I like it better when I have to follow the procedures given in the lab manual.</td>
</tr>
</tbody>
</table>

aValues indicate the averages in percentage with standard deviations over five years. Entries in bold indicate the category with the highest percentage.

Of the responses, students report little or no opinion with the following statements: the guided inquiry labs are fun to do (39 ± 8%); the guided inquiry labs are easy to do (43 ± 7%); I like to come up with my own procedure (33 ± 14%); guided inquiry labs increased my interest in Chemistry (40 ± 14%). We attribute the outcome of these responses to the additional time and effort required for the completion of the guided-inquiry lab activities.
In terms of student success, students often meet or exceed their own academic expectations for the course (Table 6.4). This can be attributed to a general positive attitude towards the guided-
inquiry laboratory activities discussed previously in addition to student experience with inquiry-based learning. The literature reports a strong correlation between attitude and achievement which indicates that positive attitudes most often leads to a higher level of achievement.\textsuperscript{113–116}

\begin{table}[!h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{Expected} & \textbf{Expected} & \textbf{Expected} & \textbf{Expected} & \textbf{Expected} \\
\textbf{"A"} & \textbf{"A-/B+"} & \textbf{"B"} & \textbf{"B-/C+"} & \textbf{"C"} \\
\hline
45.5% & 11.1% & 31.3% & 1.5% & 4.8% \\
\pm 17.9% & \pm 11.3% & \pm 11.0% & \pm 3.4% & \pm 6.6% \\
\hline
\textbf{Received} & \textbf{Received} & \textbf{Received} & \textbf{Received} & \textbf{Received} \\
\textbf{"A"} & \textbf{"A-/B+"} & \textbf{"B"} & \textbf{"B-/C+"} & \textbf{"C"} \\
\hline
48.7% & 34.1% & 12.0% & 2.9% & 1.5% \\
\pm 17.6% & \pm 9.8% & \pm 14.0% & \pm 4.5% & \pm 3.4% \\
\hline
\end{tabular}
\caption{Distribution of student grades.}
\end{table}

Note: Values indicate the averages in percentage with standard deviations over five years. The entries in bold indicate the category with the most responses.

Furthermore, students report experiencing guided-inquiry laboratory activities before their General Chemistry course at Georgetown University (Figure 6.2). In fact, the percentage of students indicating experience has steadily increased over the course of this study. This can be attributed to a greater emphasis on inquiry-based lab activities in the high school curriculum based on the recent publication of an inquiry-based laboratory manual for AP Chemistry courses in 2013.\textsuperscript{108}

\begin{figure}[!h]
\centering
\includegraphics[width=\textwidth]{student_experience.png}
\caption{Student experience with guided-inquiry laboratory activities.}
\end{figure}
Students were also surveyed on their perception of the one-week versus two-week time frames (Table 6.5). When a two-week time frame is employed, a high percentage of students report that they had more time (69%) and felt less stressed (90%) when compared to a one-week time frame. These results may provide insight into students’ responses towards the guided-inquiry laboratory activities and the workload discussed previously. We attribute students’ preference for the two-week time frame to their need for ample time to think about, analyze, and understand the material. The two-week time frame for guided inquiry lab activities engenders higher-quality and longer-lasting learning, mirroring the benefits reported by students in this study although it may limit the number of labs in the course. Our recommendation is also supported by students’ comments: “I really enjoyed the two-week guided inquiry labs. They gave me the opportunity to test out my own ideas/procedure like a real researcher/scientist…” and another student reflected on her experience stating that she appreciated the two-week lab format “since it allowed me to understand the theory behind what we were doing.”

Table 6.5. Distribution of semantic differential survey results on the time needed to complete guided-inquiry laboratory activities.a

<table>
<thead>
<tr>
<th>Statement Number</th>
<th>Left Statement</th>
<th>Agreement w/ left statement</th>
<th>No opinion</th>
<th>Agreement w/ right statement</th>
<th>Right Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>Two-weeks is enough to complete the guided inquiry labs.</td>
<td>68.8%</td>
<td>22.9%</td>
<td>8.3%</td>
<td>One-week is enough to complete the guided inquiry labs.</td>
</tr>
<tr>
<td>18</td>
<td>I felt less stressed when performing two-week labs compared to one-week labs.</td>
<td>89.6%</td>
<td>4.2%</td>
<td>6.3%</td>
<td>I felt more stressed when performing two-weeks labs compared to one-week labs.</td>
</tr>
</tbody>
</table>

aValues indicate the averages over two years. Entries in bold indicate the category with the highest percentage.

To address our second research question, students were asked how well the guided inquiry lab activities prepared them for the authentic inquiry freelance lab project (Table 6.6). Overall, students found that guided inquiry labs allow them to think creatively about the material in creating
(56%) and successfully completing (67%) the freelance lab project. Although the authentic inquiry freelance lab project introduces a level of complexity to the curriculum, the guided-inquiry lab activities gave students experience in procedure development therefore better preparing students for greater success in this endeavor. A rising junior reflected on her experience stating that “the [freelance] lab at the end of the year was… intimidating, but in retrospect, it prepared me so much for laboratory research – forming the question, designing an experimental procedure, and knowing what to do next and how to feel when the experiment failed. The [freelance] lab also involved my first poster presentation, which felt like such a huge accomplishment at the time.” A rising senior commented saying “I really enjoyed conducting the end of the semester freelance lab, where we worked with a partner to design and conduct our own experiment. It was a great experience to be able to design our own experiment on our own, and then to troubleshoot the experiment when we did not always receive the expected results. Today, I find that I apply the same lessons that I learned from completing the freelance lab to formulate my own experimental design while conducting experiments as a research assistant.”

Table 6.6. Distribution of semantic differential survey results on student opinion towards authentic-inquiry lab activities.\(^{a}\)

<table>
<thead>
<tr>
<th>Statement Number</th>
<th>Left Statement</th>
<th>Agreement w/ left statement</th>
<th>No opinion</th>
<th>Agreement w/ right statement</th>
<th>Right Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>Guided inquiry labs allowed me to think creatively about the material in creating a freelance lab project.</td>
<td>56.3%</td>
<td>31.3%</td>
<td>10.4%</td>
<td>Guided inquiry labs did not allow me to think creatively about the material in creating the freelance lab project.</td>
</tr>
<tr>
<td>20</td>
<td>I felt that guided inquiry labs prepared me well to successfully complete the freelance lab project.</td>
<td>66.7%</td>
<td>18.8%</td>
<td>12.5%</td>
<td>I didn't feel that guided inquiry labs prepared me well to successfully complete the freelance lab project.</td>
</tr>
</tbody>
</table>

\(^{a}\)Values indicate the averages over two years. Entries in bold indicate the category with the highest percentage.
Further statistical analysis of the data was performed to determine if there existed differences in responses based on gender, expected grade, and experience with guided-inquiry based laboratory activities. Table 6.7 shows the population sizes based on these groups. For each left statement on our semantic differential survey, Table 6.8 shows students’ responses (average) stratified by gender (‘male’ versus ‘female’); expected grades (‘A’ versus ‘B’); and previous experience with guided inquiry labs (‘yes’ versus ‘no’).

Table 6.7. Population sizes.

<table>
<thead>
<tr>
<th>Population</th>
<th>Size</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Male</td>
<td>57</td>
<td>112(^b)</td>
</tr>
<tr>
<td>Female</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Expected ‘A’</td>
<td>65(^c)</td>
<td>102(^d)</td>
</tr>
<tr>
<td>Expected ‘B’</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>GI Experience</td>
<td>86</td>
<td>114(^e)</td>
</tr>
<tr>
<td>GI Inexperience</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>

In further analysis, the Shapiro-Wilks test revealed that the data was not normally distributed and thus could not be tested with a t-test. Instead, the following p-values were found using the nonparametric Wilcoxon rank sum test in R, also known as a Mann-Whitney U test. The cells representing significant p-values (p < .05) reveal that it is statistically unlikely (at a less than 5% chance) that the differences between the two groups tested are due to random variation. This

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\(^b\) 3 students did not select a gender and their answers were excluded from the statistical tests.

\(^c\) 14 students selected both ‘A’ and ‘B’. These were included in the group with an expected ‘A’ grade.

\(^d\) 6 students selected that they expected a C average and 5 students did not select an expected grade average. Both groups’ responses were excluded.

\(^e\) 1 student did not indicate whether they had experience with guided-inquiry laboratory activities. Their answers were excluded from the statistical tests.
is the case for statement 7 for the male and female groups and statements 5, 13, and 15 for the ‘Expected A Average’ and ‘Expected B Average’ groups (Table 6.9).

Table 6.8. Distribution of semantic differential survey averages.a

<table>
<thead>
<tr>
<th>Statement Number</th>
<th>Males</th>
<th>Females</th>
<th>Expected “A”</th>
<th>Expected “B”</th>
<th>GI Experience</th>
<th>GI Inexperience</th>
<th>Statement Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.21</td>
<td>3.20</td>
<td>3.37</td>
<td>3.03</td>
<td>3.16</td>
<td>3.41</td>
<td>3.22</td>
</tr>
<tr>
<td>2</td>
<td>3.91</td>
<td>4.16</td>
<td>4.10</td>
<td>4.04</td>
<td>4.02</td>
<td>4.16</td>
<td>4.06</td>
</tr>
<tr>
<td>3</td>
<td>3.67</td>
<td>3.78</td>
<td>3.66</td>
<td>3.92</td>
<td>3.75</td>
<td>3.74</td>
<td>3.73</td>
</tr>
<tr>
<td>4</td>
<td>4.32</td>
<td>4.2</td>
<td>4.08</td>
<td>4.46</td>
<td>4.22</td>
<td>4.43</td>
<td>4.25</td>
</tr>
<tr>
<td>5</td>
<td>4.25</td>
<td>4.27</td>
<td><strong>4.06</strong></td>
<td><strong>4.51</strong></td>
<td>4.33</td>
<td>4.11</td>
<td>4.26</td>
</tr>
<tr>
<td>6</td>
<td>2.35</td>
<td>2.35</td>
<td>2.41</td>
<td>2.14</td>
<td>2.35</td>
<td>2.32</td>
<td>2.37</td>
</tr>
<tr>
<td>7</td>
<td><strong>2.82</strong></td>
<td><strong>3.47</strong></td>
<td>3.04</td>
<td>3.27</td>
<td>3.17</td>
<td>3.05</td>
<td>3.15</td>
</tr>
<tr>
<td>8</td>
<td>2.44</td>
<td>2.51</td>
<td>2.43</td>
<td>2.62</td>
<td>2.44</td>
<td>2.64</td>
<td>2.49</td>
</tr>
<tr>
<td>9</td>
<td>3.29</td>
<td>3.09</td>
<td>3.10</td>
<td>3.38</td>
<td>3.19</td>
<td>3.27</td>
<td>3.21</td>
</tr>
<tr>
<td>10</td>
<td>2.16</td>
<td>2.22</td>
<td>2.06</td>
<td>2.24</td>
<td>2.16</td>
<td>2.39</td>
<td>2.23</td>
</tr>
<tr>
<td>11</td>
<td>2.84</td>
<td>2.78</td>
<td>2.82</td>
<td>2.95</td>
<td>2.78</td>
<td>3.00</td>
<td>2.83</td>
</tr>
<tr>
<td>12</td>
<td>2.54</td>
<td>2.12</td>
<td>2.25</td>
<td>2.65</td>
<td>2.36</td>
<td>2.30</td>
<td>2.34</td>
</tr>
<tr>
<td>13</td>
<td>2.55</td>
<td>2.38</td>
<td><strong>2.31</strong></td>
<td><strong>2.77</strong></td>
<td>2.42</td>
<td>2.79</td>
<td>2.50</td>
</tr>
<tr>
<td>14</td>
<td>2.39</td>
<td>2.38</td>
<td>2.35</td>
<td>2.47</td>
<td>2.37</td>
<td>2.54</td>
<td>2.40</td>
</tr>
<tr>
<td>15</td>
<td>2.99</td>
<td>2.67</td>
<td><strong>2.57</strong></td>
<td><strong>3.15</strong></td>
<td>2.88</td>
<td>2.82</td>
<td>2.86</td>
</tr>
<tr>
<td>16</td>
<td>2.56</td>
<td>2.42</td>
<td>2.29</td>
<td>2.70</td>
<td>2.45</td>
<td>2.71</td>
<td>2.52</td>
</tr>
</tbody>
</table>

Note: A rating of 1 = strongly agree with left statement, 2 = moderately agree with left statement, 3 = no opinion, 4 = moderately agree with right statement, 5 = strongly agree with right statement. The bolded entries represent statistical significance at p-value = .05.
Table 6.9. P-value results from Mann-Whitney U Test in R.

<table>
<thead>
<tr>
<th>Statement</th>
<th>Gender</th>
<th>Grade</th>
<th>Guided Inquiry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9157</td>
<td>0.05535</td>
<td>0.274</td>
</tr>
<tr>
<td>2</td>
<td><strong>0.142</strong></td>
<td><strong>0.8183</strong></td>
<td>0.3761</td>
</tr>
<tr>
<td>3</td>
<td>0.7491</td>
<td>0.186</td>
<td>0.8866</td>
</tr>
<tr>
<td>4</td>
<td>0.6959</td>
<td>0.09216</td>
<td>0.3991</td>
</tr>
<tr>
<td>5</td>
<td>0.9722</td>
<td><strong>0.005293</strong></td>
<td>0.2835</td>
</tr>
<tr>
<td>6</td>
<td>0.9445</td>
<td>0.1976</td>
<td>0.8028</td>
</tr>
<tr>
<td>7</td>
<td><strong>0.006348</strong></td>
<td>0.3162</td>
<td>0.5515</td>
</tr>
<tr>
<td>8</td>
<td>0.5042</td>
<td>0.633</td>
<td>0.3997</td>
</tr>
<tr>
<td>9</td>
<td>0.3787</td>
<td>0.237</td>
<td>0.8824</td>
</tr>
<tr>
<td>10</td>
<td>0.7013</td>
<td>0.7093</td>
<td>0.3552</td>
</tr>
<tr>
<td>11</td>
<td>0.6772</td>
<td>0.733</td>
<td>0.2887</td>
</tr>
<tr>
<td>12</td>
<td>0.07176</td>
<td>0.1495</td>
<td>0.6692</td>
</tr>
<tr>
<td>13</td>
<td>0.397</td>
<td><strong>0.02014</strong></td>
<td>0.149</td>
</tr>
<tr>
<td>14</td>
<td>0.9264</td>
<td>0.6047</td>
<td>0.5518</td>
</tr>
<tr>
<td>15</td>
<td>0.1713</td>
<td><strong>0.01469</strong></td>
<td>0.9835</td>
</tr>
<tr>
<td>16</td>
<td>0.4551</td>
<td>0.1006</td>
<td>0.3671</td>
</tr>
<tr>
<td>17</td>
<td><strong>0.7997</strong></td>
<td><strong>0.2672</strong></td>
<td><strong>0.3444</strong></td>
</tr>
<tr>
<td>18</td>
<td><strong>0.1872</strong></td>
<td>0.5528</td>
<td><strong>0.9158</strong></td>
</tr>
<tr>
<td>19</td>
<td><strong>0.77</strong></td>
<td>1</td>
<td><strong>0.7965</strong></td>
</tr>
<tr>
<td>20</td>
<td><strong>0.7105</strong></td>
<td><strong>0.7376</strong></td>
<td><strong>0.6961</strong></td>
</tr>
</tbody>
</table>

The values highlighted represent statistical significance at a p-value = .05. The results in bold correspond to results run on a smaller population size and were tested with an Exact Wilcoxon rank sum test. All other results were tested with an Asymptotic Wilcoxon rank sum test.

Based on these findings, it is observed that male students prefer to create their own procedures compared to female students. Also, those students expecting an ‘A’ in the course reported a higher agreement with the following statements when compared to the students expecting a ‘B’: guided inquiry labs take a smaller amount of time to complete, guided inquiry labs helped build confidence, and guidance inquiry labs increased their interest in chemistry. No significant differences were noted when students were stratified based on prior guided inquiry lab experience.

6.4 Conclusion

In summary, an analysis of a five-year semantic differential survey strongly suggests that students report numerous benefits associated with the implementation of guided inquiry-based lab
experiments in the General Chemistry Laboratory. These benefits include a greater understanding of concepts, an increased confidence in their understanding of chemistry, and a better learning of the scientific process. These skills are also supported by student performance, reflective comments, as well as data indicating student exposure to guided-inquiry laboratory activities prior to their General Chemistry course. Furthermore, guided-inquiry lab activities can prepare students for authentic inquiry activities, and ultimately scientific research. Although students admit to spending more time, effort, thinking and analyzing in completing guided-inquiry experiments, a two-week time frame may provide the time necessary to think about, analyze, and understand the material. Overall, most of the students surveyed recommend our guided-inquiry lab format for General Chemistry courses.
CHAPTER 7. CONCLUSIONS

The synthesis of metal chalcogenide nanostructures has attracted much attention as a result of the optical, electronic, and/or magnetic properties exhibited. Our interest in the first row transition metal chalcogenides and first row lanthanide metal chalcogenides stems from their ability to exhibit magnetism. In particular, we are interested in the synthesis of iron selenide, samarium sulfide, and samarium selenide nanostructures. However, there exist several synthetic challenges in these systems because of the wide range of stable phases exhibited due to the stable divalent and trivalent metal oxidation states. Phase purity is required for application, and there exists the need to establish phase control. Additional synthetic challenges include that for structure type control, morphology control, and composition control. Given the similar stable oxidation states of iron and samarium, similar synthetic approaches were considered for the synthesis of the chalcogenide nanomaterials of interest.

This work demonstrates the ability to establish phase and structure type control for tet-FeSe, hex-FeSe, Fe₃Se₄, and FeSe₂ via the hot injection method. Of the reaction conditions investigated, precursor mole ratio largely influences the Fe₃Se₄ phase in selenium-rich conditions, whereas the FeSe phase is favored in iron-rich conditions. Ultimately, reaction time is shown to be the factor in elucidating structure type control in FeSe, where hex-FeSe is favored at shorter reaction times of five minutes and tet-FeSe is the thermodynamically stable structure type that is isolated at reaction times of at least twenty minutes. Traditionally, capping ligands are shown to influence morphology; however, we show that employing a co-solvent system of oleylamine and oleic acid can influence phase for the formation of FeSe₂. Utilizing an appropriate capping ligand solution of oleylamine and hexadecylamine is demonstrated to establish morphology control in
tet-FeSe for cubic nanoplatelets. Given the naturally layered structure of tet-FeSe, doping via intercalation is of interest and continues to be studied for establishing composition control for superconducting tet-FeSe.

Although the samarium chalcogenides exhibit similar phases, including SmX, Sm$_2$X$_3$, and Sm$_3$X$_4$, where X = S or Se, the chemistry of these materials is shown to be quite different. In fact, we demonstrate that samarium is more oxophillic than iron, and trivalent samarium is more stable than divalent samarium. This work reports the investigation of various precursors and other reaction conditions via the hot injection method, resulting in Sm$_3$X$_4$ or mixed phase systems. Given the stability of trivalent samarium, we also demonstrate its ability to act as an electron donor in doped europium selenide nanomaterials for enhancing the resulting electronic properties. At low doping levels, where Eu$_{0.90}$Sm$_{0.10}$Se, we show evidence of Sm$^{3+}$ incorporation via TEM and a shift in the diffraction peaks for a smaller cell constant.

Overall, we have learned that the chemistry of iron selenide and samarium chalcogenide nanomaterials is quite different, although similar synthetic considerations can be made to address the synthetic challenges for phase, structure type, morphology, and composition control. Finally, this work demonstrates the benefits of implementing inquiry-based learning the General Chemistry Laboratory, which can aid in strengthening the skills necessary for a successful career as a chemist.
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