NANOMATERIALS MADE OF EARTH-ABUNDANT ELEMENTS FOR PHOTOVOLTAICS

by:

Doreen Molk
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Chemistry.

Golden, Colorado
Date: ________________

Signed: ______________________
Doreen Molk

Signed: ______________________
Dr. Yongan Yang
Thesis Advisor

Golden, Colorado
Date: ________________

Signed: ______________________
Dr. David Wu
Professor and Head
Department of Chemistry and Geochemistry
Of the many types of solar cells currently under exploration, multijunction photovoltaics (MJPVs) are of the most interest due to their record-breaking solar energy conversion efficiencies (over 40%). However, MJPV device fabrication is expensive because they require a costly synthesis technique that utilizes rare elements such as gallium, arsenic, and indium. To resolve this issue, our efforts have been focused on the replacement of the thin-film materials currently employed in MJPVs with a more earth-abundant alternative, Zn-alloyed iron pyrite (Zn$_x$Fe$_{(1-x)}$S$_2$). The synthesis of Zn$_x$Fe$_{(1-x)}$S$_2$ nanoparticles is of particular interest because a nanoparticle ‘ink’ can be inserted into a roll-to-roll processor, which is an inexpensive technique of creating defect-free thin-films for electronics.

The first part of this work explores the synthesis of Zn-alloyed iron pyrite nanoparticles via the modification of a solvothermal method from the literature. The nanoparticles generated using this method at first indicated zinc-alloying was successful; yet, further studies into the electronic structure of the particles necessitated the addition of a spin-purification step to ensure only highly soluble particles remained for spin-coating deposition. Compositional and structural analysis of the particles that remained after the additional spin-purification step showed evidence of both the ZnS and FeS$_2$ phases.

The second part of this work focuses on the development of an alternative method of generating iron pyrite nanoparticles, which would also eventually be used for zinc-alloying. The two approaches focused on are a hydrothermal method in an acid-digestion bomb and a non-injection solvothermal method in an inert environment. The synthesized particles using these methods were phase-pure and did not contain any detectable quantity of other iron sulfides.
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................ iii

LIST OF FIGURES ................................................................................................................ vii

LIST OF TABLES .................................................................................................................. ix

ACKNOWLEDGEMENTS ..................................................................................................... x

DEDICATION ......................................................................................................................... xi

Chapter 1: Introduction ....................................................................................................... 12
  1.1 Statement of the Problem ......................................................................................... 12
  1.2 Single Junction Solar Cell Mechanism and Current Research ............................... 13
  1.3 Multijunction Solar Cells ....................................................................................... 15
  1.4 Zinc-Alloyed Iron Pyrite for Multijunction Solar Cells .......................................... 18
  1.5 Possible Complications When Synthesizing Zinc-Alloyed Iron Pyrite .................... 22

Chapter 2: Zinc-alloyed Iron Pyrite .................................................................................. 24
  2.1 Introduction ............................................................................................................. 24
  2.2 Methodology ........................................................................................................... 25
  2.3 Results and Discussion .......................................................................................... 27
    2.3.1 Structural Analysis by XRD ............................................................................. 27
    2.3.2 Composition Analyzed by EDX ...................................................................... 29
    2.3.3 Morphology Analysis by TEM ....................................................................... 32
    2.3.4 Investigation into Presence of Zn-S Bond by Raman and Far-IR ..................... 32
LIST OF FIGURES

Figure 1.1: Mechanism of a single junction solar cell. ................................................................. 13

Figure 1.2: Maximum efficiencies at each wavelength, as determined by William Shockley and Hans Quiesser in 1963. ................................................................................................................................. 14

Figure 1.3: Traditional 3-layer multijunction solar cell. ................................................................. 15

Figure 1.4: Theoretical efficiencies achievable as the number of junctions is increased. ...................... 16

Figure 1.5: The lattice-matched (a) and metamorphic (b) designs which are typically used in multijunction solar cells. ............................................................................................................. 17

Figure 1.6: Rock-salt crystal structure of iron pyrite. ....................................................................... 18

Figure 1.7: Comparison of cost of extraction of raw elements for semiconductors versus the amount of power generated. Both axes are normalized to silicon. ................................................................. 19

Figure 1.8: Cation replacement of Fe with Zn. .................................................................................. 20

Figure 1.9: A hypothetical curve of iron pyrite as alloying percentage with Zn is increased. ................. 21

Figure 1.10: Band gap as a function of increasing zinc composition, as calculated by Wu et al. (48). .......... 23

Figure 2.1: Iron pyrite films after sintering at temperatures between 500 and 600° C. ............................ 24

Figure 2.2: Diagram of hot solvothermal injection method developed by Law et al. in 2011. ................... 25

Figure 2.3: XRD patterns of samples with increasing Zn percentages. Black reference pattern corresponds to iron pyrite JCPDS 01-071-0053. Orange reference pattern corresponds to sphalerite JCPDS 00-001-0792. ....... 28

Figure 2.4: Elemental EDX signals as adding amount of Zn is increased from 0% to 60%....................... 30

Figure 2.5: Atomic Zn percentage by EDX (red) and Atomic S percentage over atomic metal atom percentage (blue) vs. Zn adding amount.................................................................................................................. 31

Figure 2.6: TEM images of synthesized particles with an adding amount of 0% Zn (a), 10% Zn (b), 30% Zn (c), and 50% Zn (d). ........................................................................................................................................ 33

Figure 2.7: Raman spectroscopy data for particles with increasing adding amounts of Zn, with Zn powder reference (a), sulfur powder reference (b), marcasite from ref (71) (c), and commercial iron pyrite reference (d). Samples analyzed had Zn percentages of 0% Zn (e), 10% Zn (f), and 30% Zn (g). ......................................................... 34
Figure 2.8: Far-IR analysis of samples with increasing Zn adding amount. The pyrite reference is from Law et al. (18). There is no analysis of a sample with a Zn adding amount of 50% due to a mistake in sample preparation. ...........................................................................................................................................36

Figure 2.9: UV-Vis-NIR absorbance of samples with Zn percentages increasing from 0% to 50%. ..................38

Figure 2.10: Tauc analysis for indirect band gap (a) and direct band gap (b) semiconductors using UV-Vis-NIR absorbance data shown in Figure 2.9. ...........................................................................................................39

Figure 2.11: TEM image (a) and EDX analysis (b) of sample with 20% adding amount of Zn after additional spin purification. The copper found by EDX is due to the copper TEM grid.................................................................41

Figure 2.12: XRD analysis of samples with 20% Zn added or 40% Zn added after additional spin purification.
Pyrite reference 01-079-0617 is shown in black, and sphalerite reference 00-001-0792 is shown in orange.....42

Figure 2.13: (a) XRD spectra of syntheses with 0%, 2.5%, and 5% Zn in FeS$_2$. (b) TEM image of 2.5% Zn sample.
(c) TEM image of 5% Zn sample.........................................................................................................................44

Figure 3.1: (a) Iron diethyldithiocarbamate, or Fe(DDCM)$_3$, precursor used in pyrite synthesis. (b) Non-injection solvothermal reaction set-up for pyrite synthesis in Schlenk line. .............................................................................46

Figure 3.2: XRD results of experiment N00, showing the generation of magnetite. ...........................................48

Figure 3.3: XRD Results of experiment N01, showing the generation of pyrrhotite..............................................49

Figure 3.4: XRD analysis of N13 (a) and N19 (b), showing the generation of Greigite. A small amount of pyrite is also generated in N19 ........................................................................................................50

Figure 3.5: XRD analysis of N44, showing the generation of iron pyrite...............................................................51

Figure 3.6: XRD analysis of N82, showing the generation of iron pyrite...............................................................53

Figure 4.1: PARR acid digestion bomb used in pyrite synthesis.................................................................55

Figure 4.2: XRD analysis of B00, showing the generation of large particles of iron pyrite. ............................56

Figure 4.3: XRD analysis of B47 showing generation of iron pyrite (a). SEM imaging of same experiment showing cubic particles between 100-1000 nm in size (b). ..................................................................................57
LIST OF TABLES

Table 1.1: Experimentally-determined bowing coefficients of alloyed materials in the literature........................................22

Table 2.1: Standard Energies of elements in EDX analysis. Elements shown are those that may be detectable in this synthesis. Copper is included because the grid used in measurement is made of Cu. ........................................29

Table 2.2: Band gaps determined using the linear portion of the data analyzed using the Tauc method. Data used for this analysis is taken from Figure 2.10 (a), where r=1/2.............................................................38
ACKNOWLEDGEMENTS

First, I would like to thank my advisor, Dr. Yongan Yang, for providing meaningful advice and a encouraging environment in which to conduct research. Also, for his understanding and personal guidance as I found my way in graduate school. I would like to thank my fellow group members including Jacqui Cloud, Tara Yoder, Jacob Bell, and Kevin McCann for their friendship and assistance in my research. My gratitude goes to my committee members, Dr. Ryan Richards and Dr. Stephen Boyes, for their contribution towards getting this degree.

I would also like to acknowledge Dr. Lynn Gedvilas at the National Renewable Energy Laboratory (NREL) for her assistance in the Far-IR measurements, Dr. Joey Luther at NREL for his help with the UV/Vis/NIR measurements, as well as Dr. Zhenhuan Chi at Renishaw for performing the Raman measurements.

Lastly, thank you to my family and friends who have supported me throughout my quest to get a master's degree in chemistry. I would not have made it through without your love and support. To my parents: Thank you for giving me every opportunity and for giving me the freedom to find my own path. Every success I have is due to your support and encouragement. To papa: Your relationship is so important to me, thank you for inspiring me to live a meaningful life, and for teaching me culture and selflessness. To my grandma: Thank you for your understanding, personal counsel and support. Our relationship is open and honest, and your guidance was crucial in each decision I made throughout my graduate journey. To my grandpa: Thank you for always making me laugh, and for challenging me and inspiring me to achieve great things. I am so lucky to have all of you in my life, and I love you all very much.
DEDICATION

This manuscript is dedicated to my grandparents; Leizer Molk, Helen Wurzel, and Jules Wurzel.
Chapter 1: Introduction

1.1 Statement of the Problem

People all over the world are becoming concerned with our global energy future. Not only has it been predicted that we are past our maximum global production of oil (1), but a continued dependence on fossil fuels will have negative effects on our country's future political and environmental stability. Therefore, it is important that there is a global focus on the development and implementation of renewable energies.

Of the many methods to harvest energy renewably, solar energy is of increased interest due to the excessive amounts of available energy that fall on the earth's surface in the form of light every day. In fact, the amount of solar energy that hits the earth's surface in one hour can meet the world's power needs for one year (2), making it the most abundant renewable energy resource by far. For example, there is over twenty times more solar energy than wind energy, and ten times more solar energy than geothermal; wind and geothermal being the most abundant renewable energy sources after solar (3).

The most extensively researched solar-based technology is photovoltaic (PV) cells, or solar cells, which have been in around since 1839, with the first solar-powered device was built in 1954 (4). There are many advantages to harvesting energy using a solar cell as compared with conventional methods, such as coal. First, there is no greenhouse gas emission. In addition, PVs have long lifetimes, exceeding 25 years. This is because they have no mechanical parts and as a result, require very little maintenance. Furthermore, in regards to power generation, they are also attractive because they do not require a centralized power source and they harvest energy in the middle of the day. This is advantageous because power can be generated at the time when the most energy is used, and it can be generated literally feet from the building that is utilizing it.
The material commonly used for solar cells is silicon, in large part because it is extremely abundant (it is the second most abundant element after oxygen in the earth’s crust) (5). However, the cost of producing high-purity silicon wafers is rather high. Wafers are produced using the Czochralski process, which requires an inert environment and temperatures as high as 1500°C. In addition, wafers need to be around 200 micrometers thick (6). While not fully preventing the sale of solar cells, the high cost of silicon wafer production has stunted the success of solar cells in the market, making it difficult for them to play a significant role in global energy generation. Ultimately, a new alternative to the traditional silicon solar cell is needed.

### 1.2 Single Junction Solar Cell Mechanism and Current Research

A typical silicon solar cell is shown in Figure 1.1. It involves the stacking of two doped layers of silicon on top of each other. A n-doped, or negatively-doped region is stacked on top of a p-doped, or positively-doped region. At their interface, a diode is generated that prevents the passage of electrons into the p-doped region and holes into the n-doped region. As a result, electrons will travel away from this interface, towards the cathode and eventually around the circuit in order to recombine with the holes. Thereby, a current is generated.

![Figure 1.1: Mechanism of a single junction solar cell.](image)
In a publication by William Shockley and Hans Quiesser in 1963, it was determined that this design is capable of achieving a maximum efficiency of 32% conversion of light to electricity (7). This number is determined by considering the band gap of the material, the solar spectrum, the inevitable recombination of some electrons and holes despite the attempt to separate them, and the loss of some energy as heat (blackbody radiation). The calculated efficiency as a function of band gap considering these losses is shown in Figure 1.2. The highest efficiencies can be achieved at band gaps between 1 and 1.5 eV. Silicon has a band gap of 1.1 eV, which is why it is so frequently used in PV cells (it is 85% of the current market) (6). The maximum efficiency of 32%, while much higher than most other renewable energies, still leaves much room for improvement. Furthermore, silicon commercial solar cells have only achieved efficiencies between 12-19% (8). Consequently, the energy harvested is not sufficient to justify the expensive fabrication process. As a result, researchers have continued to develop PV technology so that solar cells might be a competitive option for energy generation in the future.

![Figure 1.2: Maximum efficiencies at each wavelength, as determined by William Shockley and Hans Quiesser in 1963.](image)

The focus to improve the traditional silicon solar cell has led to the development of the multijunction PV, a clever adaptation to the typical single junction solar cell to achieve a greater maximum energy conversion efficiency. Multijunction PVs have achieved the highest energy conversion efficiency of any solar cell to date (43% in 2011, as compared to the traditional solar cell which has not yet passed 28%) (9)(10).
1.3 Multijunction Solar Cells

A multijunction solar cell involves the stacking of single junction solar cells on top of each other (Figure 1.3). Most are designed with three junctions where an efficiency of 50% is possible (11). However, as the number of gaps is increased, so is the theoretical efficiency of the device (as shown in Figure 1.4). With an infinite number of junctions, a theoretical efficiency of 85% could be achieved (using the Shockley-Quiesser limit of efficiency).

When assembling a multijunction solar cell, special attention paid to the materials used and in what order they are stacked. Each material should have a different band gap. The material utilized in the top junction has the largest band gap. In a typical triple junction cell, it will be 1.8 eV (12). As a result, this junction will only catch photons with an energy above 1.8 eV, i.e., a wavelength less than 690 nm. Photons with a longer wavelength will pass through the material unabsorbed, and will then encounter the second junction with a band gap around 1.2 eV, where photons with a wavelength shorter than 1020 nm will be absorbed. All remaining photons that are not yet absorbed into the material will encounter the bottommost junction, with a band gap of 0.7 eV. This will absorb all light in the infrared region, up to a wavelength of 1774 nm. This stacked design allows for a larger range of solar spectrum capture and an increased efficiency,
since photons are selectively filtered and absorbed in the material with optimal absorption and conversion efficiency at that wavelength \((4)\) \((9)\).

Multijunction solar cells, while much more efficient, are also much more complex to assemble. This is because the efficient movement of charge through the material, which is required for high current, is entirely dependent on whether bonding is continuous throughout the entire device \((13)\). This concern does not exist in a single junction cell, as there is only one material employed. In a multijunction, however, it is much more convoluted since each junction is made of a different material. To avoid this problem entirely, the lattice-matched design is often employed which ensures uninterrupted bonding between junctions because all materials have the same crystal structure and same lattice parameters. This design, while effective, is severely limiting to the selection of materials that can be utilized in the cell \((14)\). As a result, a metamorphic multijunction cell was developed to allow for materials of slightly different lattice parameters to be used in the same device. The metamorphic design allows for the gradual expansion of the lattice parameter over space, so as to ensure the minimal amount of bonds are broken or strained as the lattice constants evolve. As a result, charge can be transferred effectively throughout the device, despite the change in lattice parameter (Figure 1.5).

---

Figure 1.4: Theoretical efficiencies achievable as the number of junctions is increased.
To date, the most efficient solar cell is a metamorphic design with a 43% achieved conversion efficiency (9). This technology, while extremely promising, has not proceeded to commercial market because they are outrageously expensive to produce. One reason for the high cost is due to the elements used in its construction. In the most efficient multijunction PV, its top layer is made of InGaP, the middle layer is made of InGaAs, and the bottom layer is Ge. All of these elements are extremely rare, with the exception of phosphorous. Indium is the least abundant of those utilized, with an estimated 250 ppb in the earth's crust (15). Gallium and Germanium are also very expensive to extract from the earth's crust, as Gallium does not exist as a pure metal and is only at 19 ppm and Germanium is estimated to be at 1.5 ppm. Undoubtedly, the cost of simply obtaining these rare elements drives up manufacturing costs drastically. Beyond utilizing rare elements, the assembly of these cells is also very costly and involves a very energy-intensive synthesis technique called Organometallic Vapor Phase Epitaxy, or OMVPE. While capable of generating very high quality crystals, OMVPE is unattractive because it requires high temperatures, complicated reactors, and the use of toxic organometallic precursors, all of which drive up costs (16). Thus, there is a strong desire to develop a multijunction solar that utilizes earth-abundant elements.

Figure 1.5: The lattice-matched (a) and metamorphic (b) designs which are typically used in multijunction solar cells.
1.4 Zinc-Alloyed Iron Pyrite for Multijunction Solar Cells

As a solution to this cost problem, this thesis focuses on the use of zinc-alloyed iron pyrite as an alternative to the materials utilized in the metamorphic multijunction solar cell. Iron pyrite has long been researched as a potential material for PVs because it is made of abundant elements (the most common mineral in earth surface environments (17), it has adequate electronic properties and it has the potential for band gap tuning.

Pyrite has a table salt structure, or two interpenetrating fcc lattices; one occupied by iron atoms in the 2+ oxidation state, the other occupied by a sulfur-to-sulfur dumbbell. The orientation of the dumbbell convolutes the crystal structure beyond a simple cubic crystal structure, putting it into the space group \textit{Pa3} (17). This crystal structure is shown in Figure 1.6.

![Rock-salt crystal structure of iron pyrite.](image)

In the 1980's, it was proposed that iron pyrite be used as an alternative to silicon in solar cells. This is not only because it is extremely abundant and easy to extract, but because iron pyrite is a semiconductor with a band gap around 0.95 eV with a very high absorption coefficient and an sufficient minority carrier diffusion length (18). In fact, when compared with twenty-three other semiconducting materials and
silicon in particular, iron pyrite is estimated to be about ten times less expensive to obtain the mineral from the earth's crust and it is capable of generating about ten times the power per gram (Figure 1.7) (19).

Since multijunction PVs require materials of different band gaps, with each layer having a different gap, a method of band gap tuning in iron pyrite is required in order for it to be utilized in multijunction cells.

There are two methods often employed to tune the band gap of materials. The first, often referred to as quantum confinement, involves restricting the material in one dimension to within the average distance between the free electron and its corresponding hole (the Bohr radius) in one dimension. The more the material is confined, the larger the band gap. This is easily achieved in silicon and cadmium telluride, which have Bohr radii at 4.3 nm and 7 nm respectively (20). Iron pyrite, on the other hand, has a Bohr radius at 1.3 nm (21). This is incredibly small and requires particles as small as 1 nm in size, with size tunability in the range of 0.1 nm. This would be very difficult to achieve in iron pyrite and rules out quantum confinement as a method of band gap tuning.
The second method often utilized in band gap tuning is alloying. The alloying of iron pyrite would involve the random replacement of either (but not both) Fe or S atoms with another cation or anion respectively. As the degree of alloying is increased, the material should begin to take on more of the electronic, and physical properties associated with the alloying material.

There are many factors to consider when choosing an alloying element to tune the band gap of iron pyrite. First, it is most important to choose an element that can increase the band gap, since band gaps higher than 0.95 eV are required for multijunction cells. Secondly, the chosen element must be stable in the pyrite crystal structure together with the Fe and S atoms. Considering these two requirements, there are no possible elements that could be used for anion replacement when alloying iron pyrite. This is because the only elements that can form the pyrite crystal structure are Se and Te, but neither FeSe$_2$ and FeTe$_2$ has a band gap larger than iron pyrite (22). This leaves only the cation replacement approach, shown in Figure 1.8. Of all the possible metals that exist in the pyrite crystal structure, only two are reported to have a band gap larger than iron pyrite: CdS$_2$ and ZnS$_2$ (23). Ultimately, zinc is an attractive option because it is less toxic than cadmium. In addition, the lattice constant of zinc pyrite is 5.95 Å as compared to cadmium pyrite's, which is estimated to 6.30 Å (24). The lower lattice constant (zinc) is preferred since iron pyrite's lattice constant is 5.42 Å (22). It will be easier to incorporate zinc into iron pyrite if the lattice constants are closer together.

![Figure 1.8: Cation replacement of Fe with Zn.](image)
The degree of incorporation of the alloying element determines the band gap of the resultant material. However, it has been shown experimentally that it is a non-linear relationship between the band gap and the degree of alloying (25). Generally, it has been found that the band gap will first bow down to a low value, before increasing rapidly to the band gap of the alloying material. A hypothetical curve that shows this trend in the case of alloying iron pyrite with zinc is shown in Figure 1.9.

![Figure 1.9: A hypothetical curve of iron pyrite as alloying percentage with Zn is increased.](image)

The trend is mathematically modeled using equation 1.1 (26), where $E_{g,1}$ is the band gap of material 1, $E_{g,2}$ is band gap of material 2, $x$ is the ratio of the cation or anion in material 1, $E_g$ is the resultant band gap, and $b$ is the bowing coefficient. The bowing coefficient is a parameter that is determined experimentally, and describes the effect on the band gap as the alloying percentage is increased.

$$E_g = xE_{g,2} + (1-x)E_{g,1} - bx(1-x)$$

(1.1)

The literature shows that cation mixed alloys have demonstrated a bowing coefficient with a magnitude greater than the difference in band gaps of the two materials. Conversely, anion-mixed alloys generally have a bowing coefficient with a magnitude less than the difference in the band gaps. A summary of the literature in this subject is shown in Table 1.1. If it is assumed the iron pyrite also follows this trend, the band gap of iron pyrite could dip below iron pyrite's gap of 0.95 at alloying percentages of 5 or 10%, as
demonstrated in Figure 1.9. This would be extremely attractive for the use of iron pyrite in multijunction solar cells, as the bottom layer of a multijunction cell requires a band gap of 0.7 eV.

Table 1.1: Experimentally-determined bowing coefficients of alloyed materials in the literature.

<table>
<thead>
<tr>
<th>Material</th>
<th>E_AB</th>
<th>E_AC</th>
<th>E_BC</th>
<th>b</th>
<th>0&lt;b&lt;ΔE</th>
<th>b&gt;ΔE</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB_xC_1-x (anion-mixed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSe_1-x</td>
<td>3.6</td>
<td>2.6</td>
<td>0.4</td>
<td>Yes</td>
<td></td>
<td></td>
<td>(27)(28)</td>
</tr>
<tr>
<td>GaAs_xN_1-x</td>
<td>3.2</td>
<td>1.4</td>
<td>6.8</td>
<td>Yes</td>
<td></td>
<td></td>
<td>(29)(30)</td>
</tr>
<tr>
<td>ZnTe_1-x</td>
<td>3.7</td>
<td>2.3</td>
<td>3</td>
<td>Yes</td>
<td></td>
<td></td>
<td>(28)(31)</td>
</tr>
<tr>
<td>ZnO_1-x</td>
<td>3.8</td>
<td>3.6</td>
<td>3.6</td>
<td>Yes</td>
<td></td>
<td></td>
<td>(32)</td>
</tr>
<tr>
<td>CdTe_1-x</td>
<td>2.4</td>
<td>1.5</td>
<td>1.9</td>
<td>Yes</td>
<td></td>
<td></td>
<td>(33)</td>
</tr>
<tr>
<td>ZnSeTe_1-x</td>
<td>2.7</td>
<td>2.3</td>
<td>1.2</td>
<td>Yes</td>
<td></td>
<td></td>
<td>(28)(34)</td>
</tr>
</tbody>
</table>

| A_xB_1-xC (cation-mixed)  |      |      |      |      |        |      |       |
| ZnCd_1-xS                 | 3.7  | 2.5  | 0.6  | Yes  |        |      | (35)   |
| ZnCd_1-xSe                | 2.6  | 1.7  | 0.5  | Yes  |        |      | (36)(37) |
| BeZn_1-xSe                | 5.6  | 2.8  | 1.1  | Yes  |        |      | (38)   |
| GaIn_1-xN                 | 3.2  | 0.7  | 1.4  | Yes  |        |      | (39)(40)(41)(42) |
| GaIn_1-xP                 | 2.8  | 1.3  | 0.3  | Yes  |        |      | (43)   |
| GaIn_1-xAs                | 1.5  | 0.4  | 0.5  | Yes  |        |      | (44)   |
| AlGa_1-xN                 | 6.1  | 3.5  | 1.3  | Yes  |        |      | (45)   |
| CuAg_1-xCl                | 2.1  | 1.8  | 1.4  | Yes  |        |      | (46)   |

1.5 Possible Complications When Synthesizing Zinc-Alloyed Iron Pyrite

Despite the success of other alloys to tune the band gap, it has recently been suggested in two publications that the enthalpy of mixing zinc with iron pyrite is extremely high, making zinc-alloying a very difficult task. Sun et al. uses Density Functional Theory simulations to demonstrate that the large ΔH will make the bowing coefficient extremely large (47). Another publication by Wu et al. stated that the alloying of iron pyrite with zinc would result in only band gap narrowing (instead of broadening) at percentages higher than 5% (48). The predicted curve is shown in Figure 1.10. It is important to note, however, that these publications are purely theoretical and did not calculate ΔG, the true variable governing the
thermodynamic possibility of a reaction. Ultimately, these projections need confirmation via experimentation.

Another possible complication for this project is the poor performance that iron pyrite devices have demonstrated in the past, with open circuit voltages of around 0.2 V (it is expected to be close to the band gap, around 0.95 V) (49). This problem is likely the result of defects in the film. Some of the possible defects that are likely to form in a pyrite film include, but are not limited to, marcasite (m-FeS₂) inclusions, sulfur deficiencies (50), the formation of surface states (51), the presence of an amorphous phase on the surface, and oxygen substitutions for sulfur (52). Ultimately, the development of a synthesis technique that is capable of producing phase-pure pyrite could prevent the formation of these defects and solve the low voltage problem.

1.3 Research Objectives and Thesis Organization

The overall objective of this project is to synthesize and study zinc-alloyed iron pyrite for use in multijunction solar cells. In chapter 2, a hot solvothermal injection method to synthesize pure zinc-alloyed iron pyrite is examined. Chapters 3 and 4 are centered on the development of novel methods for making phase-pure iron pyrite by a non-injection solvothermal method and a hydrothermal method respectively. Conclusions and recommendations for future work are described in chapter 5.

![Figure 1.10: Band gap as a function of increasing zinc composition, as calculated by Wu et al. (48).](image)
Chapter 2: Zinc-alloyed Iron Pyrite

2.1 Introduction

There are several methods of iron pyrite synthesis in the literature that could be adapted for zinc-alloying, but the hot solvothermal injection method developed by Law et al. is attractive since it is performed in an inert environment and is capable of generating phase-pure iron pyrite nanocrystals with minimal sulfur deficiency and oxidation Figure 2.1. As stated previously, defects are detrimental to the performance of a PV device, and it is imperative that they are minimized. In addition, it utilizes an iron salt as a precursor rather than an iron/sulfur precursor which may make alloying more plausible since the iron and the chlorine will dissociate completely, leaving ions in solution before generating iron pyrite.

This method is also attractive because it generates soluble nanoparticles, or an 'ink', which can be deposited rather inexpensively using a roll-to-roll deposition method. In Law's paper, this is accomplished using a dip-coating deposition followed by high-temperature sintering. Sintering creates larger grains and as a result, there are fewer defects in the film. This solution-based film fabrication method decreases costs greatly versus the OMVPE method of making films in current multijunctions.

Figure 2.1: Iron pyrite films after sintering at temperatures between 500 and 600° C.
2.2 Methodology

The method employed to synthesize iron pyrite in this chapter is a solvothermal injection method performed in an inert environment. 10 grams of Octadecylamine (ODA, Aldrich, 90%) and 100 mg (0.8 µmol) of FeCl₂ (Alfa Aesar, 99%) are put in a 100 mL 3-neck flask, then degassed and purged three times at room temperature. The flask was then heated to 100°C and degassed for one hour. The thermocouple was kept outside of the flask initially, between the flask and the heating mantle so as to prevent leaking during degassing. Separately, a 25 mL 3-neck flask containing 100 mg sulfur (Aldrich, 99.998%) and 5 mL of diphenyl ether (Aldrich, 99%) was degassed and purged three times prior to heating to 70°C and degassing for another hour. The solution of ODA and FeCl₂ was heated to 220°C with the thermocouple inserted into the reaction flask, and the sulfur solution was injected into the flask. The mixture was then kept at 220°C for three hours and then cooled to less than a 100°C when 9 mL of chloroform was injected into the flask to quench the reaction. A diagram of this process was shown in Figure 2.2. The solid product was then washed with a mix of chloroform and ethanol in three cycles of dissolution and centrifugation. The resulting solution was then stored in an inert environment until analysis.

![Diagram of high-T injection method](Figure 2.2)

Figure 2.2: Diagram of hot solvothermal injection method developed by Law et al. in 2011.
In an attempt to incorporate zinc into the iron pyrite, an equimolar amount of FeCl$_2$ is replaced with ZnCl$_2$ up to 60%. The products were characterized using X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Raman Spectroscopy, Energy Dispersive X-Rays (EDX), and UV-Vis-NIR Spectroscopy. Samples were prepared for TEM and EDX by dropping the chloroform solution directly on a holey carbon copper TEM grid from EMS (Electron Microscope Supplies). The TEM is a Philips/FEI CM200 with an EDX addition.

In preparation for XRD and Raman, particles were re-dispersed in acetone (VWR, 99.9%), dropped on a glass slide, and the acetone was evaporated in air. This cycle was repeated until enough product remained on the slide for analysis. The X-Ray Diffractometer is a Philips X'Pert with a Cu anode. The current is set to 40 mA, the voltage is at 45 kV, and the wavelength is 1.54 Å. To prepare for SEM, the same cycle of drop-coating and evaporation that was used for XRD and Raman preparation was repeated, but on a steel stub instead of a glass slide. The SEM is a JEOL JSM-7000F.

When measuring the absorbance of a sample in the UV-Vis-NIR, the sample must be deposited as a thin-film on a substrate transparent in the Ultraviolet, Visible, and near Infrared light ranges. A uniform film is required to minimize the reflection that results from large particles and varied sample thickness. To achieve a film of this uniformity, a spin-coating method was utilized. First, the particles in chloroform were spun at 3.1 kRPM in a Thermo Scientific IEC Medilite Centrifuge for ten minutes to rid the samples of larger insoluble particles. Then, the samples were spun for ten minutes in a Thermo Scientific Sorvall Legend 14 Centrifuge at 14.7 RPM. A layer of the solubilized nanoparticles are spread out thinly on top of a quartz substrate. The slide was then spun at 500 RPM for 15 seconds and then 150 RPM for 30 seconds in a VT-100 spincoater (MTI Corp.). Following spin-coating, the ODA ligand was swapped with 1,2-ethanethiol. To achieve this, the slide was coated with a solution of 0.1 M 1,2-ethanethiol (Fluka, >98.0%) in ethanol and soaked for three minutes. To rid the sample of excess ethanethiol, the slide is soaked in pure ethanol for one minute.
This spin-coating method of deposition was repeated until visual inspection revealed sufficient absorption of light for detection in the UV-Vis/NIR spectrophotometer, a Cary 500. The range analyzed was from 3000 cm\(^{-1}\) to 300 cm\(^{-1}\). The resulting absorption profile is then analyzed using the Tauc method (53), which is a standard technique to determine the band gap for both direct and indirect semiconductors.

### 2.3 Results and Discussion

#### 2.3.1 Structural Analysis by XRD

The samples were first analyzed by XRD in order to determine whether any other phases were present. The results are summarized in Figure 2.3. All syntheses, with Zn adding amounts up to 60%, indicate only the presence of iron pyrite. However, the major peaks for Sphalerite (ZnS) match up closely with peaks (111), (220), and (311) for FeS\(_2\). There, it does not completely rule out the presence of sphalerite from these samples.

It is also important to note that generally when alloying a material, the XRD peaks will shift either to a larger or smaller 2\(\theta\), depending on whether or not the d-spacing has been decreased or increased respectively. Considering that zinc is a larger atom than iron with more electrons surrounding the nucleus, the d-spacing should increase to maintain the same crystal structure. As d-spacing increases, the peaks will shift to lower 2\(\theta\). This is in accordance with Bragg's law, or \(n\lambda = 2d\sin\theta\). In this equation by William Bragg (70), \(\lambda\) is the photon wavelength, \(n\) is an integer, \(d\) is the spacing between planes, and \(\theta\) is the angle at which the photon is hitting the sample. This shift to lower 2\(\theta\) is not apparent in our samples, but this could be because the peaks are broad due to the nanoparticle effect (the smaller the particles, the broader the peaks). So, it is possible that there is some shift but it is not apparent because the peaks are too wide to detect it.
Figure 2.3: XRD patterns of samples with increasing Zn percentages. Black reference pattern corresponds to iron pyrite JCPDS 01-071-0053. Orange reference pattern corresponds to sphalerite JCPDS 00-001-0792.
Considering the XRD data, it seems that there are three possibilities for what has been synthesized. The particles may be a) Zn-alloyed iron pyrite, b) pure FeS$_2$ (without any Zn alloyed inside), or c) FeS$_2$ with ZnS present as well.

2.3.2 Composition Analyzed by EDX

To elucidate whether zinc has successfully been alloyed into the sample, EDX was employed. EDX is useful for identifying the elements that are present in the sample, and at what quantity. A table of possible peaks and what element they correlate to is shown in Table 2.1, and the raw data is plotted in Figure 2.4. The data indicates that as the adding amount of Zn is increased, a larger presence of zinc is present by EDX. This rules out option b from our previous list of possible products from our synthesis (that the zinc has been washed away and is not present in the product at all).

Table 2.1: Standard Energies of elements in EDX analysis. Elements shown are those that may be detectable in this synthesis. Copper is included because the grid used in measurement is made of Cu.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>Energy (eV)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>K$_{\alpha_1}$</td>
<td>6.403212</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>K$_{\beta_1}$</td>
<td>7.057055</td>
<td>0.1348</td>
</tr>
<tr>
<td>Fe</td>
<td>L$_{\alpha_1}$</td>
<td>0.705</td>
<td>0.9</td>
</tr>
<tr>
<td>S</td>
<td>K$_{\alpha_1}$</td>
<td>2.307091</td>
<td>1</td>
</tr>
<tr>
<td>S</td>
<td>K$_{\beta_1}$</td>
<td>2.464086</td>
<td>0.0618</td>
</tr>
<tr>
<td>Zn</td>
<td>K$_{\alpha_1}$</td>
<td>8.637088</td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td>K$_{\beta_1}$</td>
<td>9.570467</td>
<td>0.1371</td>
</tr>
<tr>
<td>Zn</td>
<td>L$_{\alpha_1}$</td>
<td>1.012</td>
<td>0.9</td>
</tr>
<tr>
<td>Cl</td>
<td>K$_{\alpha_1}$</td>
<td>2.622087</td>
<td>1</td>
</tr>
<tr>
<td>Cl</td>
<td>K$_{\beta_1}$</td>
<td>2.815099</td>
<td>0.0806</td>
</tr>
<tr>
<td>Na</td>
<td>K$_{\alpha_1}$</td>
<td>1.041106</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>K$_{\alpha_1}$</td>
<td>0.522973</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td>K$_{\alpha_1}$</td>
<td>0.392313</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>K$_{\alpha_1}$</td>
<td>0.277</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>K$_{\alpha_1}$</td>
<td>8.048</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>K$_{\beta_1}$</td>
<td>8.905</td>
<td>0.2</td>
</tr>
<tr>
<td>Cu</td>
<td>L$_{\alpha_1}$</td>
<td>0.93</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Figure 2.4: Elemental EDX signals as adding amount of Zn is increased from 0% to 60%.
The approximate quantities of the different elements in the sample were determined from the areas under the Kα₁ peaks. The data was then used to compare the metal composition with the sulfur composition, which gives information regarding whether zinc is incorporated into the sample or present as Sphalerite. If the ratio of sulfur atom to metal atom (Fe + Zn) is near to 2:1, it is more likely that only Fe₅Zₓ_,₅S₂ is present, as ZnS should shift the ratio to 1:1. The result of this analysis for each Zn adding amount is shown in Figure 2.5. This figure also displays the quantity of Zn by EDX versus the adding amount of Zn in blue. Although not entirely consistent, there is some trend that as the adding amount of zinc increases, there is a near-linear increase in how much zinc is present in the sample and detectable by EDX. This trend also indicates that there is no saturation of zinc in the system at any one adding percentage, and that the adding amount of zinc chloride to the reaction flask can be increased as high as 60% percent without a new phase present.

Figure 2.5: Atomic Zn percentage by EDX (red) and Atomic S percentage over atomic metal atom percentage (blue) vs. Zn adding amount.
2.3.3  *Morphology Analysis by TEM*

TEM is a useful technique to reveal information about the morphology of particles, including their size and shape. TEM was performed on the 0%, 10%, 30%, and 50% syntheses, and these images are shown in Figure 2.6. There is a pseudo-spherical morphology of particles, which is consistent with the results reported by Matt Law in his 2011 publication. They also reported that particles occasionally have a hole in the center, referred to as the ‘donut-shape’. This phenomenon may also be present in our samples, which is clear in our image as well, most noticeably at the 50% synthesis (d).

The TEM images demonstrate a relatively uniform morphology of particles in the range of 8-12 nm in size, consistent in size with the Scherrer equation calculations. The images also seem to confirm that there is only one phase present, although this claim absolutely from a TEM analysis.

2.3.4  *Investigation into Presence of Zn-S Bond by Raman and Far-IR*

To shed more light on whether ZnS is present in the sample, Raman spectroscopy was utilized. Raman gives important information regarding the structural characteristics of the particles, i.e. what bonds are present in the material. Figure 2.7 compares our results to four references, marcasite (m-FeS₂), sphalerite (ZnS), sulfur (S), and pyrite (p-FeS₂). ZnS has a peak that is visible by Raman at 352 cm⁻¹, whereas iron pyrite has peaks at 344 cm⁻¹ (S-S libration), 380 cm⁻¹ (S-S stretching), and 430 cm⁻¹ (t₂g, or coupled libration and stretching). The peak for ZnS is not visible in our sample, as indicated by the gray line. The shift of all samples to smaller wavenumbers can be attributed to the fact that the reference patterns are for the bulk mineral, and the restriction of the particle growth in the nanoparticle range puts more strain on the bonds of the material, thereby increasing the lattice constant. This is a common phenomenon when analyzing nanoparticles by Raman spectroscopy (54).
Figure 2.6: TEM images of synthesized particles with an adding amount of 0% Zn (a), 10% Zn (b), 30% Zn (c), and 50% Zn (d).
Figure 2.7: Raman spectroscopy data for particles with increasing adding amounts of Zn, with Zn powder reference (a), sulfur powder reference (b), marcasite from ref (71) (c), and commercial iron pyrite reference (d). Samples analyzed had Zn percentages of 0% Zn (e), 10% Zn (f), and 30% Zn (g).
In addition, there is a systematic shift towards larger wavenumbers as the amount of Zn is increased. This could be due to an increase in the force constants as a result of zinc inclusions in the material. If zinc is incorporated into the crystal structure, the S-S bond will shorten to accommodate the larger zinc atom, which will put greater strain on the bond and increase the constant. This supports the predictions made by Tributsch et al. in 1998 (55).

Far-IR is another method by which information regarding the composition of the films can be analyzed. The signal is due to bond vibrations and is complementary to Raman spectroscopy. Iron pyrite has peaks in the Far-IR range at 408 μm, 348 μm, and 293 μm (18). Samples were prepared by the same method as was used in the UV-Vis-NIR preparation (spin purification followed by spin-coating), only the sample was deposited on a double-polished monocrystalline silicon wafer (100 orientation from Montco Silicon Technologies) instead of a quartz substrate, which is not transparent in the Far-IR range. These samples were then sent to Dr. Lynn Gedvilas at the National Renewable Energy Laboratory to be analyzed. The results are shown in Figure 2.8. Samples with a Zn adding amount from 0% to 60% were measured, with the exception of 50%, due to an error in samples preparation.

There is no hint of the expected peaks for pyrite in any of the measured samples. There is only a broad peak at 300 cm⁻¹ in the 60% Zn sample. This implies either that the films contained no pyrite or that the films were too thin to be visible by Far-IR. As a result, this data was at first dismissed for not having enough sample to give a strong Far-IR signal.

2.3.5 Electronic Properties Analyzed by UV-Vis-NIR Absorption Spectroscopy

In order to determine if zinc was successfully alloyed into the material and that consequently, the band gap was changing with increasing zinc incorporation, a band gap study was launched. The band gap was determined using a UV-Vis-NIR spectrophotometer. As discussed in 2.2, a thin film of uniform thickness is critical for obtaining reliable results using this method. To ensure that large insoluble particles that
Figure 2.8: Far-IR analysis of samples with increasing Zn adding amount. The pyrite reference is from Law et al.(18). There is no analysis of a sample with a Zn adding amount of 50% due to a mistake in sample preparation.
may contribute to unwanted reflection were not in solution prior to film deposition, samples were spun for an additional 10 minutes at a speed of 14.7 RPM prior to spin-coating. Very little of the sample is still soluble after this treatment, which was attributed to sample oxidation in air. The remaining soluble particles were then deposited using the spin-coating method on a quartz substrate.

The UV-Vis-NIR absorbance of samples prepared with Zn percentages from 0% to 60% is shown in Figure 2.9. The data was then analyzed using the Tauc method. J. Tauc observed that momentum is not conserved in the optical transitions of solids but this loss in momentum is predictable and dependant on whether the material has a direct or indirect optical transition, or band gap. To do the Tauc analysis, the energy (hv) is plotted on the x-axis and (hvα) is plotted on the y-axis. For direct band gaps, the value of r is 2 whereas for indirect, r is $\frac{1}{2}$. The linear portion of the curve on the resulting plot is then extrapolated to the x-axis, and the intercept corresponds to the band gap of the material.

The UV-Vis-NIR data was plotted with the r set to 2 and also to $\frac{1}{2}$ to ensure that all indirect and direct transitions present in the sample are detected (Figure 2.10). To find the band gaps of each adding amount, a line of best fit was put to the linear portion of the data. The equations of these lines were then used to determine the x-intercepts, which are all calculated in Table 2.2. Since iron pyrite exhibits an indirect gap, the data plotted with an r of $\frac{1}{2}$ is expected to predict the correct band gaps. This analysis proved to be correct in the case of the pure FeS$_2$ sample, which has a band gap of ~1.0 eV when plotted with an r = $\frac{1}{2}$. However, the samples with Zn added in demonstrated band gaps lower (<0.4 eV) than the pure sample. Furthermore, samples with percentages of 20%, 40%, and 50% had a sharp increase in absorbance at energies of 3.5 eV. When plotted with an r of 2, a possible second band gap at 3.5 eV becomes apparent for these three samples. This could correspond to the ZnS band gap, which is a direct transition and has experimentally been shown at 3.5-3.8 eV (56)(57). This data reinitiated the investigation into the presence of ZnS and the effect the addition spin purification might have on the system, since that was the only change in the protocol for the samples prepared for the UV-Vis-NIR versus those analyzed by XRD, Raman, and TEM.
Table 2.2: Band gaps determined using the linear portion of the data analyzed using the Tauc method. Data used for this analysis is taken from Figure 2.10 (a), where r=1/2.

<table>
<thead>
<tr>
<th>Zn percentage</th>
<th>Line of Best Fit</th>
<th>Band Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>( y = 0.3190x - 0.3276 )</td>
<td>1.027 eV</td>
</tr>
<tr>
<td>10%</td>
<td>( y = 0.2748x - 0.1314 )</td>
<td>0.4782 eV</td>
</tr>
<tr>
<td>20%</td>
<td>( y = 0.3850x - 0.2229 )</td>
<td>0.5789 eV</td>
</tr>
<tr>
<td>30%</td>
<td>( y = 0.2812x - 0.1326 )</td>
<td>0.4782 eV</td>
</tr>
<tr>
<td>40%</td>
<td>( y = 0.2137x - 0.0321 )</td>
<td>0.1502 eV</td>
</tr>
<tr>
<td>50%</td>
<td>( y = 0.2311x - 0.0878 )</td>
<td>0.3799 eV</td>
</tr>
</tbody>
</table>

Figure 2.9: UV-Vis-NIR absorbance of samples with Zn percentages increasing from 0% to 50%.
Figure 2.10: Tauc analysis for indirect band gap (a) and direct band gap (b) semiconductors using UV-Vis-NIR absorbance data shown in Figure 2.9.
The Tauc analysis of these samples led to the discovery of another band gap at \( \sim 3.5 \) eV, consistent with that of ZnS. It was previously determined from the Raman data that ZnS was not present in the samples. However, there was a slight change in the preparation in the films used for UV/Vis-NIR as compared to those samples for Raman: The addition of a 10 minutes spin at high speed followed by spin-coating of the sample onto a quartz substrate with an ethanedithiol ligand exchange. XRD and EDX had not been used to confirm the identity of the sample after spin purification because a large percentage of the sample spins out at high speed and almost all of what was remaining in solution was utilized to generate a film via spin coating. However, there was enough sample remaining of the 20% and 40% syntheses to be analyzed by XRD. Furthermore, the 20% synthesis had enough remaining to be analyzed by TEM/EDX. The TEM and EDX results are shown in Figure 2.11. TEM indicates the presence of small particles, approximately 5-12 nm in size (confirmed by the Scherrer equation). EDX, on the other hand, showed little to no iron (shown in red) in the sample whereas Zn was still detectable. This confirms the suspicion that there may be ZnS present in these samples.

The samples were further analyzed by XRD, shown in Figure 2.12, and it is clear from these XRD spectra that these samples are now almost entirely sphalerite with no pyrite present at all. This data, combined the TEM/EDX data, indicates that the additional spin purification step left only highly soluble particles of ZnS in the samples while the FeS\(_2\) particles were spun out of solution.

Experiments were then performed with 2.5% and 5% Zn added to the reaction flask, to see if zinc doping of iron pyrite was possible rather than zinc alloying. The XRD data of these syntheses is shown in Figure 2.13. Again, no peak shift is evident in these samples by XRD. The samples were then characterized using TEM/EDX, shown in parts b and c of Figure 2.13. Quantitative elemental analysis of these samples using EDX (not shown in figure) shows 14% atomic weight percentage of Zn for the 2.5% adding amount. This may indicate that this synthesis is co-generating ZnS alongside FeS\(_2\).
Figure 2.11: TEM image (a) and EDX analysis (b) of sample with 20% adding amount of Zn after additional spin purification. The copper found by EDX is due to the copper TEM grid.
2.4 Conclusions

At first, the XRD, Raman, and TEM/EDX data seemed to indicate the successful alloying of Zn into the iron pyrite particles using this solvothermal injection method. However, the UV-Vis-NIR absorbance data revealed an additional band gap around 3.5 eV for the 20%, 40%, and 50% Zn samples. The results initiated a re-checking of the UV-Vis-NIR samples (which underwent an additional twenty minute spin purification) for ZnS using XRD, Raman, and TEM/EDX. The data showed the presence of ZnS due to the higher solubility of these ZnS particles and the generation of an FeS$_2$ pellet during spin purification.
Alloying zinc into iron pyrite at percentages 10% or higher is not possible using this synthesis method. Further studies will need to be done at percentages lower than 10% to see if doping is possible; however, it seems likely that it is not possible to dope at these percentages either. Future studies should be focused on exploring the effectiveness of this synthesis using a different synthesis technique.
Figure 2.13: (a) XRD spectra of syntheses with 0%, 2.5%, and 5% Zn in FeS$_2$. (b) TEM image of 2.5% Zn sample. (c) TEM image of 5% Zn sample.
Chapter 3: Non-Injection Synthesis of Phase-Pure Iron Pyrite

3.1 Introduction

Chapter 2 explores adapting a hot solvothermal injection method to achieve zinc-alloying of iron pyrite with little success. Consequently, it would be useful to explore other methods of making iron pyrite that might be used for zinc-alloying. This chapter focuses on the development of an alternative method of synthesizing iron pyrite.

This method must be capable of generating phase-pure iron pyrite. This is because in the past, iron pyrite devices have demonstrated very low open circuit voltages, and it is thought that this problem can be solved by generating a film of iron pyrite with minimal defects. Defects affect electronic properties including band gap, carrier transport, and absorbance of photons; overall, defects can be devastating to the overall performance of the film. Furthermore, it is preferable that this method create a nanoparticle 'ink', or soluble suspension of nanoparticles. This would allow for the particles to be inserted into a roll-to-roll processor for film creation. Roll-to-roll processing is a rather inexpensive method that is already often employed for the commercial production of phase-pure films is roll-to-roll deposition.

Two methods have been published that produce an air-stable, phase-pure iron pyrite nanoparticle 'ink'. One of the two methods of making pyrite was utilized in an attempt in allow particles in Chapter 2 of this work. The second method is by a group out of the University of Nebraska Lincoln and is similarly structured to the Law method as they are both surfactant-assisted hot injection methods (58). These methods, while attractive for making a pyrite ink, also require the separate degassing and purging of two reaction flasks, and the hot injection of a sulfur solution into an iron (II) chloride solution. As a result, there is a need to uncover new methods of making phase-pure iron pyrite films that would not require a hot injection and thus, a complicated reactor when scaling for commercial use. The basis of the next
chapter of this work is the exploration of other methods of making iron pyrite that might be cheaper and which in some cases, may also potentially be a good method to generate zinc-alloyed iron pyrite.

3.2 Methodology

The principal investigator on this project has a great deal of experience in synthesizing colloidal nanoparticles in an inert environment using a non-injection method with octadecene (ODE, Aldrich, 90%) and oleic acid (Aldrich, 90%). His work on the synthesis of colloidal cadmium telluride and cadmium selenide nanoparticles was the inspiration for much of the following research (59).

This solvothermal reaction set-up is similar to that which was utilized for the Matt Law method of chapter 2, without the added step of a hot injection. A three-neck flask containing iron diethyldithiocarbamate or Fe(DDCM)$_3$ shown in Figure 3.1, sometimes elemental sulfur, and a varying ratio of ligand to solvent is connected up to the Schlenk line shown in Figure 3.1. The solution was then degassed and purged three times at room temperature and the thermocouple was placed between the heating pad and the flask. The temperature was raised to 100°C. The thermocouple cannot be placed inside the flask, since it is

![Figure 3.1: (a) Iron diethyldithiocarbamate, or Fe(DDCM)$_3$, precursor used in pyrite synthesis. (b) Non-injection solvothermal reaction set-up for pyrite synthesis in Schlenk line.](image-url)
imperative that there be no leaks to the outside environment when reaching low vacuum pressures (around 20 mTorr). The temperature inside the flask is assumed to be about 20-30°C lower than what is read on the thermocouple, so it is thought to be about 70°C inside the flask in this second degassing step. Then, the thermocouple is inserted into the flask at atmospheric pressure and the temperature is raised 220-300°C, depending on the synthesis. The solution was then held at high temperature for 3 hours, prior to cooling and subsequent purification using chloroform/ethanol mixes (as described in 2.2).

To make the Fe(DDCM)$_3$ precursor, which was chosen due to its use in the literature to make pyrite (60), 0.1 mol iron (II) chloride tetrahydrate was dissolved in methanol. In a separate flask, 0.3 mol sodium diethyldithiocarbamate (NaDDCM, Aldrich, 99.0%) was also dissolved in methanol. Then, the iron chloride solution was added dropwise to the NaDDCM. The resulting solution was then vacuum filtered, and subsequently washed with methanol. The filter paper with the desired black precipitate was then dried in the oven overnight.

The products from the synthesis were analyzed by XRD. XRD is used because it can distinguish between other iron sulfides such as Marcasite (m-FeS$_2$), Greigite (Fe$_3$S$_4$), Pyrrhotite (Fe$_{1-x}$S), and Mackawanite (FeS). All of these have crystal structure that have been resolved by XRD, which should make identification straightforward.

### 3.3 Results

The first syntheses were carried out with 71.3 mg Fe(DDTC)$_3$ (~0.1 mmol) precursor in 0.5 mL oleic acid and 6.0 mL octadecene, mimicking what was done in ref. (60). The solution was then heated to 300°C and kept at high temperature for 3 hours. The XRD spectra of this reaction (N00) is shown in Figure 3.2.
It is possible that the formation of magnetite is due to excessive heating of the reaction solution. To resolve this issue, future syntheses were done at 220°C, consistent with the Law (18) and Bi (58) syntheses. Furthermore, the ligand was switched to TOPO because the literature supports using TOPO as a ligand in pyrite synthesis (20)(58). The synthesis involved 1 mL ODE, 3 g TOPO (7.76 mmol), and 100 mg Fe(DDTC)$_3$. The resulting particles were not soluble in any organic or inorganic solvent. The XRD pattern of this synthesis (N01) is shown in Figure 3.3 and it matches closely with the compound Pyrrhotite (Fe$_{1-x}$S$_x$). This result indicated that the synthesis technique was moving in the right direction, as FeS is closer to FeS$_2$ than is Fe$_3$O$_4$.

Other ligands were then tested to see if this change could result in the generation of pyrite. Most often, it was found that the product was pyrrhotite. As a result, the focus was then shifted to changes in the solvent. It wasn't until the combination of oleylamine in octadecene that there were promising results. Oleylamine was chosen due to the success of other groups using it as a ligand in pyrite synthesis (61). The XRD characterization of this product is shown in Figure 3.3, with a greigite reference shown in green. Greigite
is indicative of a step in the right direction, as the ratio of Fe to S is closer to 1:2 than Pyrrhotite (Greigite is \( \text{Fe}_3\text{S}_4 \)). This synthesis (N13) involved 6 mL ODE, 0.1 mL oleylamine, and 0.1 mmol Fe(DDCM)_3. The temperature was set to 220°C for 6 hrs.

Furthermore, Greigite was also achieved with an equimolar ratio of octadecylamine (ODA) instead of oleylamine. Other small variations resulted more often in Pyrrhotite than in Greigite. In one of these trials, however, a sample with a mixture of iron sulfides including iron pyrite was generated. The synthesis (N19) was the same overall as N13, with the only difference being the addition of 32 mg (1.00 mmol) of powdered sulfur. This was the first time that a product with iron pyrite in it was achieved, even if only in a small percentage. The results of both N13 and N19 are shown in Figure 3.4.

Following synthesis N19, several other syntheses were performed that only yielded solely either Pyrrhotite or Greigite, with no appearance of iron pyrite. It was then realized that the lack of available sulfur in the system might be preventing the generation of iron pyrite, since iron pyrite has a higher ratio of sulfur to iron than does either greigite and pyrrhotite. This may have been the reason for the small
Figure 3.4: XRD analysis of N13 (a) and N19 (b), showing the generation of Greigite. A small amount of pyrite is also generated in N19.
amount of iron pyrite in the product of N19. The addition of excess sulfur to the system resulted in the
generation of pyrite. The synthesis (N44) called for 6 mL ODE, 0.1 mL oleylamine, 1 mmol sulfur, and
0.1 mmol Fe(DDCM)$_3$. The XRD pattern is shown in Figure 3.5. Unfortunately, it was very difficult to
duplicate the purity that was achieved in this first synthesis. Subsequent syntheses often showed some
contaminating peaks of other iron sulfides visible by XRD. In addition, it was also clear that the
oleylamine was reacting with the reaction set-up prior to heating. This was apparent due to the change in
color of the reaction solution from yellow to orange even before the addition of the metal salt. A
literature search revealed that sulfur and oleylamine will react at room temperature in air (62). To remedy
this problem, an additional step of degassing the oleylamine prior to the addition of the solid sulfur was
added to the synthesis.

The same level of purity achieved in N44 was not seen for many trials. As a result, small variations in the
molar ratio of oleylamine to ODE were also attempted to synthesize a high purity product. In addition,
oleic acid was also occasionally reintroduced into the system. Reactions still yielded a pyrite product, as
long as excess sulfur was present, with small amounts of iron sulfides present as well.

![N44 XRD](image)

Figure 3.5: XRD analysis of N44, showing the generation of iron pyrite.
Finally, it wasn't until a synthesis (N82) with 5 mL oleylamine, 1 mL oleic acid, 1.0 mmol sulfur, and 0.1 mmol Fe(DDCM)$_3$ that a product with purity equal to N44 was achieved. Judging by the width of the peaks of the XRD pattern in this synthesis, it also seems that these particles are much smaller than those generated in N44. The Scherrer equation (3.1) can be used to approximate size using XRD spectra (63).

$$d = \frac{K\lambda}{\beta\cos\theta}$$

(3.1)

The constant $K$ is related to the predicted morphology of the particle. $K$ can be between 0.89 to 0.94 but most often, a $K$ of 0.9 is used to approximate a spherical shape (64). The wavelength of the light ($\lambda$) is 0.154 nm. $\theta$ is the angle the light is hitting the material, and $\beta$ is the full-width half max of one peak in the pattern. The product of this calculation, $d$, is the diameter of the particle and turned out to be 5.9 nm.

The pure pyrite product is shown in Figure 3.6.

3.4 Conclusions

Phase-pure iron pyrite nanocrystals have been successfully synthesized using a non-injection method that involves sulfur, Fe(DDCM)$_3$, and oleylamine in ODE. The size of the particles generated in this method is estimated to be about 5.9 nm in size. The particles, despite their relatively small size as determined by the Scherrer equation, are not soluble in any tested solvents such as chloroform, carbon tetrachloride, hexane, acetone, methanol, or ethanol. The poor solubility does not permit the use of the particles in a roll-to-roll deposition method. Thus, this method needs to be further modified to create soluble nanoparticles. Also, more characterization tools other than XRD, such as TEM and Raman, are needed in order to obtain more information about size and shape of the particles.
Figure 3.6: XRD analysis of N82, showing the generation of iron pyrite.
Chapter 4: Hydrothermal Synthesis of Iron Pyrite

4.1 Introduction

Iron pyrite can also be synthesized simply with an acid-digestion bomb. This technique is attractive because it is a very scalable technique, as it a one step synthesis that does not require an inert environment. Several publications have generated iron pyrite using the hydrothermal method (60)(65); however, only one recent publication by Wadia et al. has reported to generate particles in the nano-range (61). As a result, the following work is focused on generating nanoparticles utilizing a hydrothermal synthesis method.

4.2 Methodology

The hydrothermal bomb method described in this portion of this work was developed by Qian et al. in ref (60). These particles, while pure, are rather large, about 500 nm in diameter. Another method employed by Alivisatos et al in ref (61), generates particles about 50 nm in diameter. This method is different from the Qian et al. method in that it also included a ligand in the particle synthesis. Towards the goal of elucidating a method of making an 'ink', this portion of this work is focused on adapting the Qian et al. method with the addition of a ligand.

In a typical reaction, 100 mg (0.15 mmol) of Fe(DCM)₃ and 10 mL of water were placed into a 23 mL PARR acid digestion bomb (catalog number 04-731-54, shown in Figure 4.1) with a teflon liner to protect the bomb, and reacted for 18 hours. The product was then purified using a hexane/acetone mix (it was solubilized with hexane, and precipitated out with acetone). It was then centrifuged for 3-5 minutes at 3.1 krpm. The supernatant was poured off, and this process was repeated two more times. The particles were then dispersed in acetone and deposited on a quartz slide for analysis by XRD.
4.3 Results

First, the parameters as described in section 3.1.2 were attempted in order to assure that these results from the literature could be duplicated prior to making adaptations. The results of this synthesis (B00) are shown in Figure 4.2.

Once the purity of the literature synthesis was repeated, ligands were added to the system to restrict the size of these resulting particles. Some ligands that were added to the synthesis were TOPO, oleylamine, Cetyl trimethylammonium bromide (CTAB), or DDT (dodecanethiol). The introduction of almost all of these ligands into the system resulted in the generation of pyrrhotite alongside pyrite when analyzed by XRD. Only one ligand, TOPO, had a pure pyrite product. Consequently, several trials were performed varying the amount of TOPO. One such trial (B47), involving 70 mg TOPO, 120 mg Fe(DDCM)₃ in 12 mL of H₂O at 180°C is shown in Figure 4.3. A SEM image of the particles generated by this method is shown in part b of Figure 4.3. The particles appear to be cubic and in the size range (100-1000 nm) as the original synthesis (B00).

Figure 4.1: PARR acid digestion bomb used in pyrite synthesis.

55
Phase-pure iron pyrite particles has been successfully synthesized using an acid-digestion bomb. TOPO was the best ligand to control the size of pyrite particles, as its presence in the system does not result in the generation of other iron sulfides alongside pyrite. In future studies, there needs to be further modifications to the reaction conditions in order to achieve some size control of particles. In addition, it would be beneficial to use TEM to gain more information about the size, shape, and morphology of particles.

Figure 4.2: XRD analysis of B00, showing the generation of large particles of iron pyrite.
Figure 4.3: XRD analysis of B47 showing generation of iron pyrite (a). SEM imaging of same experiment showing cubic particles between 100-1000 nm in size (b).
Chapter 5: Conclusions and Recommendations for Future Work

5.1 Zn-Alloyed Iron Pyrite

Towards the goal of fabricating earth-abundant nanomaterials suitable for use in MJPVs, we explored a solvothermal method to generate Zn-alloyed iron pyrite with a band gap that is tunable dependant on the zinc composition. The obtained nanocrystals were systematically characterized by XRD, TEM, EDX, Raman, Far IR, and UV-Vis-NIR. The results showed the co-existence of ZnS and FeS$_2$ in the products with no evidence of Zn$_x$Fe$_{1-x}$S$_2$ nanocrystals. Considering this, and the literature suggesting that the mixing of zinc with iron pyrite has an extremely high ΔH, future studies will be focused on the incorporation of zinc into iron pyrite at x<0.10. Although these nanoparticles will not be useful for multijunction solar cells as they will not demonstrate the desired band gaps, it is fundamentally interesting to determine the feasibility of alloying iron pyrite with zinc at any quantity.

5.1.1 Zinc Incorporation at x<0.10

The experiments shown in need further characterization to explore if zinc incorporation was successful. Ideally, the samples could be analyzed using XAS (X-Ray Absorption Spectroscopy) and EXAFS (Extended X-Ray Absorbance Fine Structure). XAS provides more accurate and precise measurements on the elemental compositions. EXAFS can tell if the existent Zn is indeed in the pyrite lattice, based on the first and second layer of coordination atoms from S and Fe. Dr. Tsu-Chien Weng at SLACS is willing to help with these two experiments.

However, XAS and EXFAS require that the products be soluble. To improve solubility, the ligand could be swapped with an additional annealing step could be added. The ligand octadecanethiol has demonstrated some potential to improve solubility of the sample, as our samples remained soluble for 2 weeks after treatment with octadecanethiol for 2 hours at 50°C in chloroform in an inert atmosphere.
However, further characterization needs to be performed in order to confirm the ligand was actually exchanged. Infrared spectroscopy would be very useful for this determination, as it would elucidate which bonds are present in the ligand.

In another approach to exchange the ligand, the products of the synthesis will first undergo one ethanol/chloroform or hexane/acetone wash prior to immersion in pure oleic acid at 220°C for 1-3 hours. The particles will then subsequently undergo several washes using the same non-polar/polar solvent mix. This annealing step should ensure the replacement of the octadecylamine ligand with oleic acid, which will better passivate the nanoparticles and make them more soluble in organic solvents such as hexane, chloroform, and toluene. All characterizations will be performed after the products have been submitted to the same purification processes.

5.1.2 Core-shell Growth Followed by Annealing

In another approach to generating zinc-alloyed iron pyrite, FeS$_2$ nanoparticles are grown and then used as seeds for the shell growth of a ZnS or ZnS$_2$ shell. The particles are then annealed at high temperature in order to mix the two phases and generate Zn$_x$Fe$_{1-x}$S$_2$. This core-shell growth method has been widely used in the literature (66).

5.1.3 Annealing Pre-made Iron Pyrite Particles in the Presence of Zinc Precursor

Alternatively, zinc-alloyed iron pyrite could be generated by annealing the pre-made FeS$_2$ nanoparticles in the presence of zinc precursors such as zinc oleate, zinc chloride, and dimethyl zinc. In theory, the zinc precursor would first replace the iron atoms on the surface and then thermally migrate into the nanocrystals.
5.2 Iron Pyrite Nanoparticle Synthesis

In Chapter 4, two methods of synthesizing phase-pure iron pyrite nanoparticles were developed. The non-injection solvothermal method called for 5 mL oleylamine, 1 mL oleic acid, 1.0 mmol sulfur, and 0.1 mmol Fe(DDCM)$_3$, and the solution was heated to 220°C for 3 hours in the Shlenck line. The final synthesis using the hydrothermal method called for 70 mg TOPO, 120 mg Fe(DDCM)$_3$ in 12 mL of H$_2$O at 180°C. Unfortunately, products from both syntheses were not soluble in any of the tested organic solvents such as hexane, toluene, and chloroform. This is critical in order for this product to be used in a roll-to-roll deposition method. Therefore, all future work should be focused on making these particles soluble.

5.2.1 Adjusting the Reaction Temperature, Time, and Ratio of Reagents

Temperature, ligand to solvent ratio, and length of synthesis are some of the reaction parameters that have been widely used in the literature to control the nanocrystal size, structure, and morphology. For example, soluble iron pyrite nanowires were obtained using a reaction time of only 2 hours in ref (67). Also, reaction time was used to control the size of the CdSe particles generated in ref (59).

5.2.2 Varying the Iron Precursor

Also, a different iron precursor might be necessary to generate iron pyrite nanocrystals. The precursor utilized in our method is iron diethyldithiocarbamate; however, there is potential to get smaller or more soluble particles if iron precursor is different. There are several publications that have utilized a variety of single-source precursors to generate iron pyrite or other sulfur-rich iron sulfides. For example, one group utilized Fe(DDCM)$_2$(Phen), Phen being 1,10-Phenanthroline (68). Another publication utilized 1,1,5,5-tetraalkyl-2-thiobiurets (69).
REFERENCES CITED

(1) Brown, L. R. Plan B 3.0: Mobilizing to Save Civilization; 2008; p. 50.


