Crystal structure, electronic structure, and physicochemical characterization of diamond-like semiconductors prepared by high-temperature solid-state synthesis

Kimberly Ann Rosmus

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CRYSTAL STRUCTURE, ELECTRONIC STRUCTURE, AND PHYSICOCHEMICAL CHARACTERIZATION OF DIAMOND-LIKE SEMICONDUCTORS PREPARED BY HIGH-TEMPERATURE SOLID-STATE SYNTHESIS

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Submitted to the Bayer School
of Natural and Environmental Sciences

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In partial fulfillment of the requirements for
the degree of Doctor of Philosophy

By
Kimberly Ann Rosmus

August 2014
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CHARACTERIZATION OF DIAMOND-LIKE SEMICONDUCTORS PREPARED BY
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ABSTRACT

CRYSTAL STRUCTURE, ELECTRONIC STRUCTURE, AND PHYSICOCHEMICAL CHARACTERIZATION OF DIAMOND-LIKE SEMICONDUCTORS PREPARED BY HIGH-TEMPERATURE SOLID-STATE SYNTHESIS

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Kimberly Ann Rosmus

August 2014

Dissertation supervised by Dr. Jennifer A. Aitken

Diamond-like semiconductors (DLSs) have structures that are derived from cubic or hexagonal diamond. The compositions of DLSs are predictable and flexible allowing for properties to be tuned to target technological applications. The fields of photovoltaics, thermoelectrics, and nonlinear optics (NLO) are in need of materials with improved efficiencies for practical devices. Toward the goal of discovering advanced materials, systematic studies of DLSs allowing for the elucidation of structure-property and composition-property relationships were carried out. Here, in-depth structural, physicochemical, and computational studies have been performed on several DLSs to correlate the crystal and electronic structure with the physicochemical properties.

The DLSs, α-Cu₂ZnSiS₄, β-Cu₂ZnSiS₄, Cu₂CdSiS₄, Cu₂CdSnS₄ and AgInSe₂:Mn were synthesized via high-temperature, solid-state synthesis. Synchrotron X-ray powder
diffraction (XRPD) of Cu$_2$ZnSiS$_4$ revealed the presence of two polymorphs, α-Cu$_2$ZnSiS$_4$ and β-Cu$_2$ZnSiS$_4$. Rietveld refinement of synchrotron XRPD and single crystal X-ray diffraction data showed that α-Cu$_2$ZnSiS$_4$ crystallizes with the wurtz-stannite structure, in the noncentrosymmetric space group Pmn2$_1$. The new polymorph, β-Cu$_2$ZnSiS$_4$, crystallizes with the wurtz-kesterite structure, in the noncentrosymmetric space group Pn. X-ray photoelectron spectroscopy of the α/β-Cu$_2$ZnSiS$_4$ sample and Cu$_2$CdSiS$_4$ verified the expected oxidation states of the ions. The calculated electronic structures (ES) of all of the studied materials indicate that the top of the valence band is dominated by the hybridization of the Cu/Ag-$d$ and chalcogen-$p$ states. The second-order nonlinear optical susceptibility ($\chi^{(2)}$), 62±3 pm/V, the third-order nonlinear optical susceptibility, ($\chi^{(3)}$), [(8.0±2.0)$\times$10$^4$ pm$^2$/V$^2$], and the laser-damage threshold (LDT), 0.2 GW/cm$^2$, for Cu$_2$CdSnS$_4$ are similar to AgGaSe$_2$, a benchmark infrared (IR) NLO material. While $\chi^{(2)}$ and $\chi^{(3)}$ of α/β-Cu$_2$ZnSiS$_4$ are lower, the material outshines benchmark IR NLO materials in LDT (2.0 GW/cm$^2$). These results align with the ideas that a higher degree of covalency leads to larger NLO susceptibility, while a wider bandgap leads to better LDT. Rietveld refinements using laboratory XRPD data indicated that Ag$_{1.2x}$Mn$_x$InSe$_2$ (x=0-0.07) and Ag$_{0.95}$Mn$_{0.05}$InSe$_2$ are single-phase materials, where manganese was found to occupy the Ag (4a) site. The incorporation of manganese provides a simple means for physical property tuning, and likely represents a general mechanism for the substitution of silver ions with higher valence dopants in this system.
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1. An Introduction to Diamond-like Semiconductors

1.1 Introduction

Diamond-like semiconductors (DLSs) are materials with bandgaps between zero and approximately four electron volts that crystallize with structures resembling diamond. The crystal structures of DLSs are derived from either the hexagonal or cubic forms of diamond. DLSs are commercially available for use in various applications, such as light-emitting diodes, photovoltaics, and nonlinear optics. Additionally, there are several types of applications where DLSs are believed to be relevant, such as spintronics and thermoelectrics, but have not yet been realized in practical applications. In the areas of photovoltaics and nonlinear optics the diamond-like materials that are currently being used contain several non-earth-abundant elements, which are costly. Additionally, the currently used materials in these areas are not as efficient as desired, thus new materials are constantly being prepared and their properties investigated to find new device materials with improved efficiencies. Until now, many multinary diamond-like materials have yet to be prepared and numerous others, although they have been prepared, have not been fully investigated. This dissertation focuses on α-Cu$_2$ZnSiS$_4$, β-Cu$_2$ZnSiS$_4$, Cu$_2$CdSiS$_4$, Cu$_2$CdSnS$_4$, and AgInSe$_2$. The syntheses of all of these DLSs, except for β-Cu$_2$ZnSiS$_4$, have been previously reported in the literature; however, this dissertation work focuses on an in-depth study of the crystal structure, electronic structure, and physicochemical characterization of each. In the process of these in-depth studies the new phase, β-Cu$_2$ZnSiS$_4$, and the manganese substituted AgInSe$_2$ phases were discovered and characterized.
1.2 Fundamentals of Diamond-Like Semiconductors

The diamond-like crystal structures are based on either cubic closest packing, such as that found in cubic diamond, or hexagonal closest packing, like the hexagonal lonsdaleite structure.\textsuperscript{22,23} However, DLSs not only vary in anion packing but also in cation ordering. For example, hexagonal derived DLSs with space groups of $Pn$, $Pna2_1$, and $Pmn2_1$ only differ in the arrangement of the cations within the hexagonally closest packed anion array. DLSs are known as normal valence compounds, meaning that the elements will accept, donate, and/or share electrons to achieve a full octet. Using these different means to acquire or donate electrons, the bonding in these materials can be ionic, iono-covalent, or covalent. For the compounds to be DLSs, there are four guidelines that must be followed.\textsuperscript{22-24}

The first guideline states that the average number of valence electrons for each atom must equal four,\textsuperscript{22,23} just as carbon has four valence electrons. For this study, compounds of the formulae I-III-VI$_2$ and I$_2$-II-IV-VI$_4$ were explored, where the Roman numeral is the number of valence electrons that the atom brings to the compound and the subscripts represents the number of each atom per formula unit. The ternary I-III-VI$_2$ compounds have sixteen valence electrons between the four atoms, giving an average of four valence electrons per atom. The quaternary I$_2$-II-IV-VI$_4$ compounds have thirty-two valence electrons between eight atoms that averages to four valence electrons per atom. Eq.1.1 can be used to determine the average number of valence electrons, $V_{Eave}$:

$V_{Eave} = \frac{v_{etot}}{n_{ions}}, \quad (\text{Eq. 1.1})$

where $v_{etot}$ is the total number of valence electrons per the cations and anions, and $n_{ions}$ is the total number of cations and anions in the formula unit.
The second guideline is that the number of valence electrons per anion, \( \text{VE}_A \) must be eight, thus the octet of each anion is achieved, see Eq 1.2.\textsuperscript{22,23} For the ternary I-III-VI\(_2\) materials there are sixteen valence electrons and two anions, resulting in \( \text{VE}_A = 8 \). The quaternary I\(_2\)-II-IV-VI\(_4\) compounds have thirty-two valence electrons and four anions, thus providing eight electrons per anion. Equation 1.2 can be used to calculate \( \text{VE}_A \).

\[
\text{VE}_A = \frac{\text{ve}_{\text{tot}}}{n_{\text{anions}}}, \quad (\text{Eq. } 1.2)
\]

The total number of valence electrons per the cations and anions is expressed as \( \text{ve}_{\text{tot}} \), and \( n_{\text{anions}} \) is the total number of anions in the formula unit.

The third guideline is that all of the ions must be tetrahedrally coordinated.\textsuperscript{24} Some authors of earlier work state that Pauling’s first rule, the radius ratio rule, can be used as a guideline.\textsuperscript{22,23} The ratio is calculated by dividing the radius of the cation, \( r^+ \), by that of the anion, \( r^- \). Pauling stated that “A coordinated polyhedron of anions is formed about each cation, the cation-anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio.”\textsuperscript{24} A radius ratio in the range of 0.25-0.414 predicts a coordination number of four (Table 1.1). However, Brunetta et al. reported that the radius ratios between ions in many diamond-like compounds do not fall within that range.\textsuperscript{25} This is not surprising considering that when Pauling devised this range, the materials that he considered were primarily oxides and highly ionic compounds. Sulfides and selenides are much softer ions and are known to be more ionic-covalent in their bonding with metal cations. Nonetheless, the carbon atoms within diamond are tetrahedrally coordinated, thus the diamond-like structures must have all ions in a tetrahedral coordination as well.
Table 1.1. Selected radius ratios used to predict coordination polyhedra.\textsuperscript{24}

<table>
<thead>
<tr>
<th>Polyhedron</th>
<th>Coordination Number</th>
<th>Minimum Radius Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedron</td>
<td>4</td>
<td>0.225</td>
</tr>
<tr>
<td>Octahedron</td>
<td>6</td>
<td>0.414</td>
</tr>
<tr>
<td>Cube</td>
<td>8</td>
<td>0.732</td>
</tr>
</tbody>
</table>

The last guideline is Pauling’s second rule, the electrostatic valence sum rule, which states that the charge of the anion should be compensated by the nearest neighbor cations, allowing for both global and local electroneutrality.\textsuperscript{24} The strength of the electrostatic valence bond going to each corner of the polyhedron is shown as:

\[ s = \frac{z}{v}, \quad \text{(Eq. 1.3)} \]

where \( s \) is the strength of the electrostatic valence bond, \( z \) is the electric charge of a cation, and \( v \) the coordination number of the cation. To calculate the charge surrounding the anion \( (\zeta) \), the equation becomes:

\[ \zeta = \Sigma_i \left( \frac{z_i}{v_i} \right) = \Sigma_i s_i. \quad \text{(Eq. 1.4)} \]

For example, in the compound \( \alpha\text{-Cu}_2\text{ZnSiS}_4 \), each \( S^{2-} \) ion is surrounded by two \( Cu^{1+} \) ions, one \( Zn^{2+} \) ion, and one \( Si^{4+} \) ion, where each \( Cu^{1+} \) gives \( s = \frac{1}{4} \), \( Zn^{2+} \) gives \( s = \frac{1}{2} \), and \( Si^{4+} \) gives \( s=1 \), resulting in a \( \zeta \) of 2. The +2 charge is compensated by the charge on the sulfur that is -2. Pauling’s second rule is used as a guideline, as even Pauling stated that Eq. 1.4 is not anticipated to satisfy all crystals, but most will satisfy approximately. If the anion is not compensated, the difference needs to be balanced within the structure through structural distortions.\textsuperscript{24} For example, if the absolute value of \( \zeta \) is less than the absolute value of the charge of the anion, the cations will be more strongly attracted to the anion, thus the bonds will be shortened. However, if the absolute value of \( \zeta \) is greater than the absolute value of the charge of the anion, then the bonds will be elongated. In either case,
a stable compound may still result; yet, the structure will not be perfectly diamond-like but rather similar to the diamond-like structure with distortions.

**Table 1.2. Formulae for DLSs.**

<table>
<thead>
<tr>
<th>Binary</th>
<th>Ternary (1 cation)</th>
<th>Ternary (2 cations)</th>
<th>Quaternary (1 cation)</th>
<th>Quaternary (2 cations)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-VII</td>
<td>III$_3$-IV$_2$-VII</td>
<td>I-IV$_2$-V$_3$</td>
<td>I-IV-V-VI</td>
<td>I-III-IV$_2$-V$_4$</td>
</tr>
<tr>
<td>II-VI</td>
<td>III$_2$-IV-VI</td>
<td>II-IV-V$_2$</td>
<td>II-III-V-VI</td>
<td>II-III$_2$-IV-V$_4$</td>
</tr>
<tr>
<td>III-V</td>
<td>II$_2$-V-VII</td>
<td><strong>I-III-VI$_2$</strong></td>
<td>II-III-IV-VII</td>
<td>I-II$_2$-III-VI$_4$</td>
</tr>
<tr>
<td>IV-IV</td>
<td>III$_2$-IV-VII$_2$</td>
<td>I$_2$-IV-VI$_3$</td>
<td>I-III-V-VII</td>
<td><strong>I$_2$-II-IV-VI$_4$</strong></td>
</tr>
<tr>
<td></td>
<td>II$_4$-III-VII$_3$</td>
<td>I$_3$-V-VI$_4$</td>
<td>I-II-VI-VII</td>
<td></td>
</tr>
</tbody>
</table>

Using these guidelines, a finite but plentiful number of compounds can be proposed using various cations and anions. Table 1.2 has the formulae for binary, ternary, and quaternary DLSs, where the bold formulae indicate those that are focused on in this dissertation. There are ten formulae for ternary DLSs and nine formulae to achieve quaternary DLSs. Computationally, Zeng et al. predicted 75 possible ternary DLSs with the formula I-III-VI$_2$ and 225 possible compounds with the formula II-IV-V$_2$. Quaternary DLSs of the formula I$_2$-II-IV-VI$_4$, for example, can be realized with I being lithium, copper, or silver, II being manganese, iron, cobalt, nickel, zinc, cadmium, or mercury, IV being silicon, germanium, or tin, and VI being sulfur, selenium, or tellurium. Thus, I$_2$-II-IV-VI$_4$ DLSs have flexibility in composition with a possibility of 189 combinations, leading to tunable properties that may be desirable for potential applications. In 1981, Brian Pamplin pointed out the importance of investigating DLSs when he stated, “The list is not endless but evidently many man years of work on basic crystal growth and characterization remain to be done.” He also stressed that a record was needed to note successful, as well as unsuccessful preparations of DLSs. Additionally, he remarked that even if only some of the predicted diamond-like materials
were to form “adding in further solid solutions and polytypes we may safely say that there are a thousand adamantine phases [DLSs] from which to choose device material.”

1.3 Structure

In Figure 1.1, a progression of structure-types from diamond to binary, ternary, and quaternary diamond-like structures are shown with those based on cubic closest packing on top and hexagonal closest packing on the bottom. All structures of a particular branch of the structure-family tree have the same arrangement of anions; however, the cation ordering varies between each, which can prove to be a challenge when solving and refining a crystal structure if the cations are isoelectronic and/or of similar size. The structure-types for the cubic progression are diamond, zinc blende or sphalerite (binary), chalcopyrite/Cu$_2$GeSe$_3$/famatinite (ternary), and stannite or kesterite (quaternary). The structure-types of the hexagonal progression are lonsdaleite, wurtzite (binary), β-NaFeO$_2$/Li$_2$SiO$_3$/enargite (ternary), and wurtz-stannite or wurtz-kesterite (quaternary). The structure-type progression for DLSs was first revealed by Parthé and Goryunnova. They both wanted to further diamond-like structure research by determining the occurrence of the multitude of crystal structure-types, as well as provide a course for future investigations. While Parthé and Goryunnova published a broad view of DLSs, Shay and Wernick focused on the chalcopyrite structure-type with the formulae of I-III-VI$_2$ and II-IV-V$_2$. 
Figure 1.1. An example transition of structures from all carbon (IV) in diamond/lonsdaleite to the binary (II-VI), ternary (I-III-VI$_2$) and quaternary (I$_2$-II-IV-VI$_4$) diamond-like structures with anions and cations, where the cubic closest packing structure on the top are shown down the a-axis are above, and hexagonal closest packing structures on the bottom shown down the c-axis are below.

1.4 Previous Work with DLSs

Most of the materials presented here have been previously prepared with some type of characterization performed; therefore, it is necessary to summarize those findings.

1.4.1 Cu$_2$ZnSiS$_4$

The lattice parameters of Cu$_2$ZnSiS$_4$ were first reported in 1967 using X-ray photographs.$^{35}$ Nitsche et al. demonstrated that iodine vapor transport could be used to
synthesize single crystals of quaternary chalcogenides of the type I$_2$-II-IV-VI$_4$, where I= Cu, II= Sn, Cd, Fe, Mn and Ni, IV= Si, Ge and Sn, and VI= S and Se; however, only the lattice parameters were reported. The lattice constants for Cu$_2$ZnSiS$_4$ were found to be $a= 7.40$ Å, $b= 6.40$ Å, and $c= 6.08$ Å and Nitsche et al. proposed that the structure should be wurtzite-like. In 1974, Schäfer and Nitsche reported a survey on lattice data and structure-types of quaternary DLSs with the formula Cu$_2$-II-IV-VI$_4$, where II= Mn, Fe, Co, Ni, Zn, Cd, Hg, IV= Si, Ge, Sn, and VI= S, Se. At that time, out of 42 possible combinations, only 22 existed. Until this point, the structure-type of Cu$_2$ZnSiS$_4$ was reported to be wurtzite-like. In this new report, Schäfer and Nitsche assigned the wurtz-stannite structure-type to Cu$_2$ZnSiS$_4$. Additionally, they reported that the wurtz-stannite structure is favorable when IV=Si, except for Cu$_2$CoSiS$_4$ and Cu$_2$FeSiS$_4$. Schleich et al. reported some electrical properties in 1997, where Cu$_2$ZnSiS$_4$ was found to be an insulator with a bandgap of 3.25 eV. Then in 2005, the lattice parameters were reported again; but, this time from indexing a powder diffraction pattern. Matsushita et al. explored Cu$_2$-II-IV-VI$_4$ compounds, where II= Zn, Cd, IV= Si, Ge, Sn, and VI= S, Se, Te, to determine the melting points, lattice constants, and bandgaps as well as to correlate those values to the mean atomic weight of the compounds. In that work Cu$_2$ZnSiS$_4$ was again synthesized via iodine vapor transport. The lattice constants for Cu$_2$ZnSiS$_4$ were found to be $a= 7.435$ Å, $b= 6.396$ Å, and $c= 6.135$ Å. In more recent works by Levcenco et al., single crystals of Cu$_2$ZnSiS$_4$ were also prepared via iodine vapor transport. Levcenco and coworkers reported several band gaps for the compound, ranging from 2.97 to 3.41 eV, using polarization-dependent piezoreflectance (PzR), surface photovoltage (SPV) spectroscopy, and electrolyte electroreflectance (EER).
measurements. Additionally, Levcenco et al. used photoluminescence and Raman scattering to study emission and vibrational properties and Hall measurements revealed that Cu$_2$ZnSiS$_4$ shows p-type semiconductor behavior. Yet despite eight previous studies, some of the physicochemical characterization of this material is still lacking, for example nonlinear optical properties, and all of the studies above were noted to be performed on only the wurtz-stannite-type Cu$_2$ZnSiS$_4$.

1.4.2 Cu$_2$CdSiS$_4$

Cu$_2$CdSiS$_4$ was first synthesized in 1967 by Nitsche, Sargent, and Wild via transport reactions with iodine in the gas phase; the lattice parameters (a = 7.58 Å, b = 6.44 Å, and c = 6.17 Å) and structure-type (wurtzite-like) were reported. Later in 1972, a full analysis of the crystal structure was published; Cu$_2$CdSiS$_4$ along with Cu$_2$CdGeS$_4$, at that time, were the first quaternary compounds known with a hexagonal close-packing of sulfur atoms. Cu$_2$CdSiS$_4$ was found to crystallize with the wurtz-stannite structure in the noncentrosymmetric hexagonal space group P$mn2_1$ with lattice parameters of a = 7.598(8) Å, b = 6.486(6) Å, and c = 6.26(1) Å. The structure-type was confirmed in 1974 by Schafer and Nitche. The melting point of Cu$_2$CdSiS$_4$ was found to be 978 °C in 1999 by Piskach et al. However, since 1999, no new information has been reported for Cu$_2$CdSiS$_4$, although the compound is often cited in publications, appearing only as an entry in tables of diamond-like materials, where its space group and lattice parameters are listed. Some of the basic properties of Cu$_2$CdSiS$_4$, such as bandgap remain unknown.

1.4.3 Cu$_2$CdSnS$_4$

The first report of Cu$_2$CdSnS$_4$ was by Nitsche et al. in 1967, where the structure was proposed to be tetragonal with a stannite-like space group with lattice parameters of
a= 5.58 Å and c= 10.82 Å. In 1974, Schäfer and Nitsche reported the structure to be stannite with lattice parameters of a = 5.586 Å and c = 10.834 Å. The crystal structure of the naturally occurring mineral cernyite, Cu$_2$(Cd$_{0.37}$Zn$_{0.33}$Fe$_{0.29}$Mn$_{0.005}$)SnS$_4$, which is relatively close to the formula of Cu$_2$CdSnS$_4$, was solved and refined by J. T. Szymnski in 1978. Cernyite was found to crystallize with the stannite structure in the noncentrosymmetric cubic space group I-42m with lattice parameters of a = 5.487(2) Å and c = 10.848(3) Å. The IR and Raman spectra were reported in 1991. In 1998, Piskach et al. determined the melting point of Cu$_2$CdSnS$_4$ to be 905 °C. The compound was reported in the space group I-4 in 2000, but this report is likely in error. This compound has been studied for potential applications in solar cells since 1977, where Wagner et al. determined Cu$_2$CdSnS$_4$ to be a p-type semiconductor with a bandgap of 1.16 eV. Quaternary DLSs with the formula Cu$_2$-II-IV-VI$_4$, where II=Mn, Fe, Co, Zn, Cd, Hg, IV=Si, Ge, Sn, and VI=S and Se have potential applications in thin film solar cells due to being structurally related to CuIn(Ga)Se$_2$, having suitable bandgap energies (1.1-1.5 eV) and possessing high absorption coefficients (10$^4$ to 10$^5$ cm$^{-1}$). Cui et al. synthesized Cu$_2$CdSnS$_4$ as nanorods and reported the valence states of each element using X-ray photoelectron spectroscopy (XPS). The nanorods were found to have a bandgap of 1.4 eV, and showed a promising photoresponse on a thin film, thus this material has potential to be used as the absorber layer in thin film solar cells. Cao et al. synthesized Cu$_2$CdSnS$_4$ solvothermally producing nanoparticles that were analyzed using X-ray powder diffraction (XRPD), transmission electron microscopy (TEM), scanning electronic microscopy coupled with energy dispersive spectroscopy, XPS, and UV-Vis spectroscopy. XRPD and TEM data of the sample showed the high quality of the
crystals. The charges of the ions were verified using XPS.\textsuperscript{53} The bandgap was also found to be 1.35 eV, which is within the range to be of practical use in solar cell applications.\textsuperscript{53} Despite this strong interest in the compound, the single crystal X-ray structure of pure Cu\textsubscript{2}CdSnS\textsubscript{4} has not been previously determined, and some of the properties of the bulk material, such as second harmonic generation response and third harmonic generation response, have not been assessed.

1.4.4 AgInSe\textsubscript{2}

AgInSe\textsubscript{2} is the most well researched compound of those investigated in this work. AgInSe\textsubscript{2} is of interest for technological applications, such as near IR nonlinear optics, optical detectors, Schottky diodes and solar cells.\textsuperscript{54,55} The potential of this compound for these applications is based on its optical and electrical properties, e.g., direct bandgap (~1.2 eV), high optical absorption (~10\textsuperscript{-5} cm\textsuperscript{-1}), capability of pn-control, and relatively high mobility.\textsuperscript{56-60} However, there have been relatively few reports concerning AgInSe\textsubscript{2} in comparison to CuInSe\textsubscript{2}, even though all of the characteristics of the silver-containing compound are better than those of today's commercially available CuInSe\textsubscript{2}-based materials. When the CuInSe\textsubscript{2}-based materials undergo chemical substitutions, the properties have been shown to improve.\textsuperscript{61,62} Therefore, substitutions in the AgInSe\textsubscript{2} system can be exploited to render the above characteristics, which are advantageous for photovoltaic devices, even more attractive. Toward this goal, Yamada et al. deposited thin films of Ag(In\textsubscript{1-x}Ga\textsubscript{x})Se\textsubscript{2} onto glass substrates.\textsuperscript{63} Hall measurements revealed that the films showed n-type conduction.\textsuperscript{63} In addition, the bandgap of the thin film solar cell was found to be 1.7 eV, with a total-area efficiency of 7.3\%.\textsuperscript{63} Toward the goal of improved thermoelectrics, Wang et al. recently substituted Zn on the Ag site in AgInSe\textsubscript{2} and found
a ZT value of 1.05 ± 0.12 at 815 K, which is larger than the ZT value of the undoped AgInSe₂ (ZT= 0.34 at 724 K). With these new found improvements and the potential use for solar cell applications, as well as thermoelectrics, additional work needs to be completed to determine the full potential of substituting AgInSe₂.

1.5 Structure Determination

As stated earlier, DLSs can differ in both closest packing type and the arrangement of the cations within the anion array. This cation ordering difference can create challenges in the structure solutions and refinements using laboratory X-ray diffraction instrumentation when the cations are of similar size or even more so when elements are isoelectronic and having nearly identical X-ray scattering factors. If two materials differ in space group, but the unit cell parameters are relatively similar, the Bragg reflections will be close in terms of position, but will differ slightly in intensities due to the different cation ordering. However, the space group with less systemic absences will have additional peaks. These additional peaks, if they have weak intensities, may be very difficult to discern from the background in laboratory data. Additionally, if the additional peaks are close to the peaks that both space groups share, then the peaks of each space group may not be resolved using laboratory data. For example, when considering XRPD patterns for structures with the space groups Pn and Pmn2₁, the space group Pn will have two peaks at some locations in 2θ°, whereas Pmn2₁ will have only one peak. The difference between those two space groups cannot be determined through laboratory XRPD data because the resolution is not sufficient. Therefore, high resolution synchrotron X-ray powder diffraction can be attained for these
materials from national laboratories. This data will allow for the slight peak variation to be revealed.

To fully analyze XRPD, Rietveld refinements are carried out using GSAS/EXPGUI.\textsuperscript{65,66} Hugo Rietveld designed the first computer program to analyze entire powder diffraction patterns in 1967.\textsuperscript{67,68} The Reitveld method, also referred to as whole pattern fitting, uses a least-squares refinement to reduce the difference between the entire observed pattern and the entire calculated pattern taking into account specimen, instrument, and structure effects. This method has advantages compared to other quantitative XRPD analysis methods that do not take into account the entire diffraction pattern. The Rietveld method refines site occupation factors, instrument effects, and specimen effects.\textsuperscript{69} Additionally, overlapping peaks and preferred orientation can be modeled.\textsuperscript{69} Lastly, laboratory and synchrotron X-ray diffraction data plus neutron data can be used in the refinements.\textsuperscript{69} On the other hand, this method requires high-quality data and decent starting models. Using this program, crystal structures of the compounds in the sample, if known, are used as starting models. However, if the compound is unknown, then the crystal structure of another supposedly similar compound may be used as a starting model and refined. On the positive side, the Rietveld method can account for the different crystal structures that may be in the sample, which produce overlapping peaks, by inputting the lattice parameters, space group, and atomic coordinates of each structure and refining their phase fractions. The shape of the peaks, which correlates to particle size, can be modeled using Gaussian and Lorentzian terms.\textsuperscript{69} Additionally, the instrument factors and specimen features, such as sample transparency, sample displacement, and preferred orientation, are accounted within the calculated model.
Furthermore, site occupancy parameters can be refined for compounds with partial occupancies and/or chemical substitutions. The method is time intensive; however, it is imperative for determining which phase(s) is(are) in a sample. For example, Ag$_2$CdGeS$_4$ was reported to crystallize in the orthorhombic, noncentrosymmetric space group $Pmn2_1$; however, Brunetta et al. used Rietveld analysis of synchrotron X-ray powder diffraction to determine that Ag$_2$CdGeS$_4$ crystallizes in the orthorhombic, noncentrosymmetric space group $Pna2_1$. Brunetta et al. stated that the structure refined from synchrotron data was valid, even if the structure refined from single crystal X-ray diffraction data had not been determined. Structure-property and composition-property correlations can only be fully realized when the crystal structure of a material is definitively known. However, when single crystals are not formed or when chemical substitutions are being performed, Rietveld analysis allows for phase identification but more important, structural refinement using the powder diffraction data.

1.6 Potential Properties

1.6.1 Photovoltaics

Solar cells provide an alternative and renewable energy source that can decrease the amount of carbon-based power. CuInS$_2$ (CISu) and CuInSe$_2$ (CIS) are I-III-VI$_2$ DLSs that have attractive photovoltaic properties. Solar cells based on these materials, CuIn$_{1-x}$Ga$_x$S$_2$, also known as CIGS, are commercially available for use in solar cell applications today. Solopower, Ascent Solar Technologies, Inc., and Manz AG are just a few companies that sell CIGS solar cells. Solopower produces a product called Solopanel® SP1, where there is a thin film of CIGS on a flexible stainless steel sheet, giving 12.5% efficiency. A thin film of CIGS was tested at the National Renewable
Energy Laboratory in March 2014, resulting in an efficiency of 20.5% ± 0.6%. What is unattractive about these materials is that CIS, CISu, and solid solutions based on these materials, such as CIGS, are fabricated with a substantial amount of indium. It is estimated that, even with a 70% recovery factor, indium could be completely mined out in 66 years. Therefore, researchers must work to produce lower-cost, indium-free solar cells, preferably containing earth-abundant elements. Additionally, materials with improved efficiencies are imperative in order for solar energy to account for a larger portion of the US energy needs.

Cu$_2$ZnSnS$_4$ (CZTS) is a quaternary DLS that has been recently proposed as a suitable alternative to CIGS solar cells due to its properties, for example the bandgap, being similar to that of CIS and CISu. The high abundance and low toxicity of Zn and Sn are some of the reasons that make CZTS an attractive alternative. Another attractive feature of CZTS is that like CIS, CISu, and CIGS, its fabrication process can be carried out with a thin layer of nanocrystals using less material and ultimately decreasing the cost. CZTS has, thus far, exhibited 8.5% ± 0.2% efficiency in solar power conversion, although, the theoretical efficiency limit is 32.2%. Therefore, quaternary DLSs, once thought to be complicated, exotic materials are finding a renewed interest in photovoltaics due to their promising physical properties.

1.6.2 Thermoelectrics

Thermoelectric (TE) devices use semiconductors to convert electricity into thermal energy or to recover waste heat and convert it into electrical power. TE materials are being investigated as another alternative energy source. However, in order for TE devices to realize their full potential and make a much larger impact in today's
world, a higher efficiency is needed for applicability such as in large-scale, solid-state refrigeration (home refrigeration), large scale cooling, and power generation.\textsuperscript{74} For solid-state refrigeration, a TE device works by the Peltier effect, which occurs when an electrical current is applied across a TE junction of a material generating a temperature gradient (Figure 1.2, left).\textsuperscript{75} This effect is exploited in the use of TEs in portable solid-state refrigerators or car seat heaters and coolers.\textsuperscript{73,76} The Seebeck effect occurs when a temperature gradient is applied across a TE junction of a material resulting in a voltage that is proportional to the temperature difference (Figure 1.2, right).\textsuperscript{77} TE devices that function based on the Seebeck effect can harvest energy from waste heat, such as heat from the exhaust of a car.\textsuperscript{73,74} In order to assess the potential of a TE material for applications, the dimensionless figure of merit, ZT, of the material is determined by:

\[ \text{ZT} = \left[ \frac{\sigma \times S^2}{\kappa_{\text{tot}}} \right] \times T, \quad \text{(Eq. 1.5)} \]

where \( \sigma \) is the electrical conductivity, \( S \) is the Seebeck coefficient, \( \kappa_{\text{tot}} \) is the total thermal conductivity, and \( T \) is the absolute temperature. \( \kappa_{\text{tot}} \) is the sum of the lattice thermal conductivity (\( \kappa_{\text{latt}} \)) and the electronic thermal conductivity (\( \kappa_e \)). To have a high ZT value, the thermal conductivity should be small, while the electrical conductivity and the Seebeck coefficient should be sufficiently large. In order to use a solid-state TE material for two-phase refrigeration, which is currently being conducted with liquid coolants, a ZT value around 9 would be required, yet most of the best TE materials have ZTs between 1 and 2.\textsuperscript{78}
DLSs that are currently being investigated for their TE properties have a ZT of around 1 and below. The ternary DLS Cu$_2$SnSe$_3$ has a ZT value of 0.5 at 850 K; however, like photovoltaics where substitution increases efficiency, substitution can also increase the ZT value. For example, the indium substituted Cu$_2$SnSe$_3$, Cu$_2$Sn$_{1-x}$In$_x$Se$_3$, showed an increase in ZT to 1.14 at 850 K. Additionally, excess copper in the I$_2$-II-IV-VI$_4$ formula increases the ZT value. The quaternary DLS CZTS has a ZT value of 0.039 at 700 K, but with excess copper, Cu$_{2.1}$Zn$_{0.9}$SnS$_4$, the ZT value increases by over an order of magnitude to 0.36 at 700 K. The structural and chemical flexibility of DLSs, makes these compounds attractive as TE materials.

1.6.3 Nonlinear Optics

1.6.3.1 Second Harmonic Generation

Since the discovery of second harmonic generation (SHG), where the frequency is doubled and the wavelength is halved (Figure 1.3, top), in quartz utilizing a ruby laser by Franken et al. in 1961, researchers have been invested in developing new and improved nonlinear optical (NLO) materials. Some of the criteria for forming an ideal SHG material are: noncentrosymmetric crystal structure, large second-order NLO
susceptibility, extreme optical transparency, environmental stability, large laser-damage threshold (LDT), large crack-free single crystals, high thermal stability, and low cost. While there are several attractive NLO crystals for use in the visible and near-IR regions,\textsuperscript{14,15} there are fewer options for use further in the IR\textsuperscript{16,17} and no one material offers radiation in the entire region. Improved NLO materials for applications in the IR region are essential to advancing telecommunications, biomedical imaging, and diagnostics, such as the detection of trace gases.\textsuperscript{80-82}

DLSs provide a reliable route to attractive SHG materials, as the compositions are predictable and the structures are inherently noncentrosymmetric, since all of the MS\textsubscript{4} tetrahedra align in one direction.\textsuperscript{22,23} Additionally, DLSs provide chemical flexibility that can be exploited to tune properties, such as phase matching and refractive index.\textsuperscript{83-85} Indeed DLSs dominate the list of current benchmark IR NLO materials.

**Table 1.3. Properties for commercially available ternary DLS IR NLO materials.\textsuperscript{86}**

<table>
<thead>
<tr>
<th>Property</th>
<th>ZnGeP\textsubscript{2}</th>
<th>AgGaSe\textsubscript{2}</th>
<th>AgGaS\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point</td>
<td>1298 °C</td>
<td>998 °C</td>
<td>1002 °C</td>
</tr>
<tr>
<td>Transparency Range</td>
<td>0.7-12 μm</td>
<td>0.8-17 μm</td>
<td>0.5-11 μm</td>
</tr>
<tr>
<td>Phase Matchability</td>
<td>λ ≥ 1100 nm</td>
<td>λ ≥ 3100 nm</td>
<td>λ ≥ 1800 nm</td>
</tr>
<tr>
<td>$\chi^{(2)}$</td>
<td>150 pm/V</td>
<td>66 pm/V</td>
<td>36 pm/V</td>
</tr>
<tr>
<td>Laser Damage Threshold (incident λ, pulse width)</td>
<td>60 MW/cm\textsup{2} (10.6 μm, 100 ns)</td>
<td>25 MW/cm\textsup{2} (2.05 μm, 50 ns)</td>
<td>10 MW/cm\textsup{2} (1.06 μm, 20 ns)</td>
</tr>
</tbody>
</table>

The ternary DLSs, AgGaSe\textsubscript{2}, AgGaS\textsubscript{2}, and ZnGeP\textsubscript{2}, among others, are commercially available NLO materials for use in the IR region (Table 1.3). While these NLO crystals have shown attractive properties in the mid-IR region each material suffers drawbacks. For operating a 2 μm-pumped optical parametric oscillator (OPO) between 2 and 8 μm, ZnGeP\textsubscript{2} is an excellent material because it is transparent and phase matchable.
at 2 μm and has a high second-order nonlinear optical susceptibility, $\chi^{(2)}$, value of 150 pm/V, yet the material is limited at longer $\lambda$ due to the onset of multiple photon absorption around 8.5 μm. Therefore, in the region from ~9-11 μm, AgGaSe$_2$ is the material of choice for frequency doubling with a CO$_2$ laser; however the material is plagued by two photon absorption (TPA) and does not have adequate birefringence for 1 μm phase matching. AgGaS$_2$ is phase matchable at 1 μm, albeit with a relatively lower $\chi^{(2)}$ value of 36 pm/V; however, the crystals are susceptible to surface damage, due to the very low LDT resulting from TPA.

New materials are showing potential in IR NLO applications. For example, Ba$_8$Sn$_4$S$_{15}$ has wide optical transparency, a $\chi^{(2)}$ of 23.92 pm/V and a LDT that is ~26× AgGaS$_2$ when irradiated with a 1.064 μm laser; but, it is non-phase matchable (NPM) at 2.05 μm. NaAsSe$_2$ shows strong SHG response, but is non-phase matchable at 1.58 μm. The ACd$_4$In$_5$Se$_{12}$ (A=Rb, Cs) compounds exhibit wide optical transparency ranges and excellent SHG responses, ~35-40× AgGaS$_2$ at 2.05 μm, but are also non-phase matchable at 2.05 μm. Due to drawbacks with even new materials, there is still a need for further research into producing improved IR NLO materials.

### 1.6.3.2 Third Harmonic Generation

A material exhibits third harmonic generation (THG) when an incident wavelength is passed through a material and the resulting wavelength is one third of the incident wavelength and the frequency is tripled. (Figure 1.3). While SHG materials are used in frequency mixing setups to access wider frequency ranges, THG materials can greatly advance processing speeds. An important difference to note between SHG and THG is that for a material to generate a SHG response, it must have a
noncentrosymmetric crystal structure; however, a noncentrosymmetric structure is not a prerequisite for a THG response. Materials that are centrosymmetric or noncentrosymmetric may generate a THG response. THG materials are attractive in applications, such as all-optical switching and optical image processing in the visible and IR.\textsuperscript{91}

![Second Harmonic Generation](image)

![Third Harmonic Generation](image)

Figure 1.3. Schematic of an example of a SHG (top) and THG (bottom) response using a wavelength at 1064 nm.

1.6.3.3 Determination of NLO Properties

1.6.3.3.1 Type I Phase Matchability

A number of properties need to be measured to determine the eligibility of a material for NLO applications; one of the most important criteria is phase matchability, which is wavelength dependent. The phase matchability is determined by measuring the SHG counts versus particle size for a particular wavelength. If the SHG counts increase with increasing particle size then the candidate material is phase matchable, whereas if the SHG counts decrease with increasing particle size, the material is non-phase matchable at that incident wavelength.\textsuperscript{92} If a material is found to be non-phase matchable at a particular wavelength, it is possible that it may be phase matchable at a different
incident wavelength. Phase matching can be thought of in a simplistic manner, such that when waves are traveling through different planes of multiple crystals in a powder sample and they are constructively interfering with each other, the result is that the SHG response will continue to grow (Figure 1.4, top). However, non-phase matching can be thought of as deconstructive interference, where the waves that are travelling through various planes of many crystals in a powder sample are cancelling each other, hence there is a decrease in SHG response (Figure 1.4, bottom).

![Constructive and Deconstructive Interference](image.png)

**Figure 1.4.** A simplistic example of constructive (top) and deconstructive (bottom) interference of waves.

**1.6.3.3.2 \( \chi^{(2)} \) Determination**

To determine the \( \chi^{(2)} \) of a material, first the phase matchability must be determined. As stated before, phase matching occurs when the SHG response increases with increasing particle size, therefore, the largest particle will have the largest SHG response. Thus, it will be necessary to measure the material with the largest particle size.
with various incident wavelengths. Conversely, for non-phase matchable materials, the SHG counts for the smallest particle size will be measured at multiple incident wavelengths.

For a material to be an attractive candidate as a NLO material, it needs to possess a high $\chi^{(2)}$. To measure the nonlinear optical susceptibility, first the sample being assessed for SHG or THG response will need to be compared to a reference material in a region where both exhibit phase matching. AgGaS$_2$ is phase matchable when the incident wavelength is greater than 1800 nm, whereas AgGaSe$_2$ is phase matchable when the incident wavelength is greater than 3100 nm. Therefore, if a sample was phase matchable at a wavelength of 2000 nm, then AgGaS$_2$ would be the better reference material. When the reference material is known, the SHG counts as a function of SHG wavelength can be used to determine the $\chi^{(2)}$ of the material. This is performed in the static range, where both the reference and sample are phase matchable with minimal absorption effects, by taking the square root of the average of the SHG counts for the sample, dividing by the average SHG counts of the reference and then multiplying by the $\chi^{(2)}$ of the reference.

1.6.3.3.3 $\chi^{(3)}$ Determination

The third-order nonlinear optical susceptibility, $\chi^{(3)}$, is found in a similar fashion as $\chi^{(2)}$. The $\chi^{(3)}$ is determined by taking the square root of the average THG counts for the sample and then dividing by the average THG counts of the reference, multiplying by the $\chi^{(3)}$ of the reference, multiplying by the coherence length of the reference and dividing by the coherence length of the sample. The coherence length is the particle size that shows the largest THG response when THG counts versus THG wavelength is plotted.
1.6.3.3.4 Laser Damage Threshold (LDT)

The LDT is another measurement that needs to be performed so that a material can be evaluated as a potential candidate for NLO applications. This measurement is important in determining the laser intensity at which the material will start to degrade. The LDT is determined by increasing the laser intensity and measuring the corresponding SHG counts. LDT significantly depends on the pulse width of the laser and the incident wavelength. The intensity data is then fit to a line, which represents the maximum SHG case where fundamental depletion is absent. Where the data deviates from this line indicates the laser intensity at which laser damage occurs.

Designing materials with improved NLO properties, such as phase matchability, SHG, THG, and LDT, is imperative for the future of laser devices, so that the drawbacks will continue to decrease, thus radiation in the entire IR region will be more accessible. The more criteria the potential NLO materials meet, the more practical that material will be in laser devices thus advancing industrial, medical, and military laser applications.

Recently, the Aitken laboratory has begun to study quaternary DLSs in order to elucidate their phase matchability, SHG, THG, and LDT properties. In 2009, Lekse et al. reported the SHG response for the quaternary DLSs, Li$_2$CdSnS$_4$ and Li$_2$CdGeS$_4$. The resulting SHG responses were 100 times and 70 times that of α-quartz, respectively, using a fixed 1064 nm Nd:YAG incident laser. In 2014, Brant et al. published the SHG response and LDT for Li$_2$CdGeS$_4$ using a tunable laser, where the $\chi^{(2)}$ was found to be 51.1 pm/V and the LDT was found to be ~4.0 GW/cm$^2$. The NLO properties, SHG, THG, LDT, are dependent on wavelength and these broadband studies show great potential for these materials to be used in NLO applications. Due to this type of material
being comparable to or better than the commercially available materials, continued research on quaternary DLSs is warranted. Furthermore, knowledge of the bandgap, can help predict the $\chi^{(2)}$ and LDT, where narrow bandgaps suggest a high $\chi^{(2)}$ with a low LDT, whereas conversely, wide bandgaps often result in the opposite. However, high NLO susceptibility and LDT are not communally restricted, as was observed for Li$_2$CdGeS$_4$. Thus, a systematic study in correlating bandgap, nonlinear susceptibilities, and LDT in diamond-like materials is essential in future design strategies.

### 1.7 Conclusion

This research focuses on the correlation between the crystal structure, electronic structure, and physicochemical properties of the quaternary DLSs, $\alpha$-Cu$_2$ZnSiS$_4$, $\beta$-Cu$_2$ZnSiS$_4$, Cu$_2$CdSiS$_4$, Cu$_2$CdSnS$_4$, and the ternary DLS AgInSe$_2$ substituted with manganese. Each of these materials (except for $\beta$-Cu$_2$ZnSiS$_4$) was previously known; however, this study will show that only the surface was scratched; there was much remaining to be investigated. A central strategy of this work is the utilization of a battery of different characterization tools through which the structure-property relationships can be elucidated in DLS materials. Systematic and in-depth studies used to correlate structure-property and composition-property relationships in DLS materials can eventually provide enough necessary information to one day target specific materials for particular applications making exploratory synthesis less of a need. Regarding DLSs, Pamplin stated “[The] crystal growth and characterization should continue in as many laboratories as possible.” However, if more predictive tools besides just determining if a particular compound will exist can be formulated; materials can be selectively synthesized for specific applications.
1.8 References


**2014**, 26, 3045-3048.

2. The single crystal Structure of Cu$_2$ZnSiS$_4$

2.1 Introduction

Cu$_2$ZnSiS$_4$ was prepared as crystals via iodine vapor transport reactions as early as 1967$^{96}$; however, only lattice parameters were reported. Using the same synthetic method to prepare Cu$_2$ZnSiS$_4$, Yao et al. reported infrared spectrum of this compound.$^{97}$ Alternatively, Cu$_2$ZnSiS$_4$ can be synthesized by grinding stoichiometric amounts of the elements and transferring them in a vibrational mill multiple times during the heating process.$^{98}$ More recently, the band gap of the title compound has been reported.$^{99}$ In this paper, Cu$_2$ZnSiS$_4$ was prepared as relatively small single crystals using a simple high-temperature solid-state synthesis.

2.2 Experimental

Cu$_2$ZnSiS$_4$ was prepared via high-temperature solid-state synthesis. Stoichiometric ratios of the elements were weighed and then ground for 30 min in an argon-filled glovebox using an agate mortar and pestle. The sample was placed into a graphite crucible, which was then inserted in a 12 mm outer diameter fused-silica tube. The tube was flame sealed under a vacuum of 10$^{-3}$ mbar and transported to a computer-controlled furnace. The sample was heated to 1000 °C in 12hrs, held at 1000 °C for 168 hrs and then cooled at 7.5 °C/hr to room temperature. When removed from the furnace, dark rod-like crystals of approximate size 0.13 x 0.07 x 0.6 mm were found under a light microscope.
2.3 Results and Discussion

Cu$_2$ZnSiS$_4$ possesses the wurtz-stannite structure type\textsuperscript{100} like that of Li$_2$CdGeS$_4$, Li$_2$CdSnS$_4$,\textsuperscript{101,102} and Cu$_2$CdSiS$_4$.\textsuperscript{103} The asymmetric unit can be observed in Figure 2.1. Cu$_2$ZnSiS$_4$ has a diamond-like structure, where every cation is tetrahedrally coordinated with sulfur anions. The bond lengths for M—S range from 2.3170 (7)-2.3426 (7) Å for M=Cu, 2.322 (1)-2.3650 (7) Å for M=Zn, and 2.131 (1)-2.143 (3) Å for M=Si (Table 2.6). Every MS$_4$ tetrahedron points in the same direction along the crystallographic b-axis rendering the structure noncentrosymmetric (Figure 2.2). When viewed down the c-axis, the ions are aligned in rows where each cation alternates with the sulfur anions (Figure 2.3).

Figure 2.1. Assymetric unit of Cu$_2$ZnSiS$_4$ using 95% probability thermal ellipsoids.

Figure 2.2. Polyhedral view down the b-axis of Cu$_2$ZnSiS$_4$ with sulfur anions as the corners of each tetrahedron.
Figure 2.3. Cu$_2$ZnSiS$_4$ viewed along the c-axis showing a 3-dimensional honeycomb structure where the atoms are aligned in rows with each cation alternating with sulfur anions. Color code: Cu - green, Zn - blue, Si - red, and S - yellow.

Recently second harmonic generation for a couple of compounds of this structure type, Li$_2$CdGeS$_4$ and Li$_2$CdSnS$_4$, have been reported on powder samples.$^{101,102}$ Therefore it is of interest to further study Cu$_2$ZnSiS$_4$.

Table 2.1. Crystal Data

<table>
<thead>
<tr>
<th>Cu$_2$S$_4$SiZn</th>
<th>$F$(000) = 332</th>
</tr>
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<tbody>
<tr>
<td>$M_r = 348.78$</td>
<td>$D_x = 3.964 \text{ Mg m}^{-3}$</td>
</tr>
<tr>
<td>Orthorhombic, $Pmn2_1$</td>
<td>Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ Å}$</td>
</tr>
<tr>
<td>Hall symbol: P 2ac -2</td>
<td>Cell parameters from 3127 reflections</td>
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<tr>
<td>$a = 7.4374$ (1) Å</td>
<td>$\theta = 3.2$–$32.2^\circ$</td>
</tr>
<tr>
<td>$b = 6.4001$ (1) Å</td>
<td>$\mu = 12.77 \text{ mm}^{-1}$</td>
</tr>
<tr>
<td>$c = 6.1394$ (1) Å</td>
<td>$T = 296$ K</td>
</tr>
<tr>
<td>$V = 292.24$ (1) Å$^3$</td>
<td>Rod, blue</td>
</tr>
<tr>
<td>$Z = 2$</td>
<td>$0.13 \times 0.07 \times 0.06 \text{ mm}$</td>
</tr>
</tbody>
</table>
Table 2.2. Data collection

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Bruker SMART ApexII diffractometer</td>
<td>1078 independent reflections</td>
</tr>
<tr>
<td>Radiation source: fine-focus sealed tube</td>
<td>1023 reflections with $I &gt; 2\sigma(I)$</td>
</tr>
<tr>
<td>graphite</td>
<td>$R_{int} = 0.021$</td>
</tr>
<tr>
<td>$\varphi$ and $\omega$ Scans scans</td>
<td>$\theta_{max} = 32.9^\circ$, $\theta_{min} = 3.2^\circ$</td>
</tr>
<tr>
<td>Absorption correction: multi-scan SADABS (Sheldrick, 2002)</td>
<td>$h = -11 \rightarrow 11$</td>
</tr>
<tr>
<td>$T_{min} = 0.290$, $T_{max} = 0.500$</td>
<td>$k = -9 \rightarrow 9$</td>
</tr>
<tr>
<td>5153 measured reflections</td>
<td>$l = -9 \rightarrow 9$</td>
</tr>
</tbody>
</table>

Table 2.3. Refinement Information

<table>
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<th>Description</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Refinement on $F^2$</td>
<td>Secondary atom site location: difference Fourier map</td>
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<tr>
<td>Least-squares matrix: full</td>
<td>$w = 1/[\sigma^2(F_o^2) + (0.0067P)^2 + 0.2702P]$</td>
</tr>
<tr>
<td>$R[F^2 &gt; 20(F^2)] = 0.020$</td>
<td>$\sigma = 0.001$</td>
</tr>
<tr>
<td>$wR(F^2) = 0.051$</td>
<td>$\Delta p_{max} = 0.72 \text{ e Å}^{-3}$</td>
</tr>
<tr>
<td>$S = 1.14$</td>
<td>$\Delta p_{min} = -1.01 \text{ e Å}^{-3}$</td>
</tr>
<tr>
<td>1078 reflections</td>
<td>Extinction correction: SHELXL, $F_c^\epsilon = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{1/4}$</td>
</tr>
<tr>
<td>44 parameters</td>
<td>Absolute structure: Flack$^{105}$</td>
</tr>
<tr>
<td>1 restraint</td>
<td>Flack parameter: 0.02 (1)</td>
</tr>
<tr>
<td>Primary atom site location: structure-invariant direct methods</td>
<td></td>
</tr>
</tbody>
</table>

Special details

**Geometry.** All estimated standard deviations (esds) (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used
when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of F^2 > 2sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

**Table 2.4 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).**

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U_{iso}^*/U_{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1</td>
<td>0.24741 (3)</td>
<td>0.17426 (4)</td>
<td>0.33723 (8)</td>
<td>0.0133 (1)</td>
</tr>
<tr>
<td>Zn1</td>
<td>0.0000</td>
<td>0.34747 (7)</td>
<td>0.84124 (15)</td>
<td>0.0211 (1)</td>
</tr>
<tr>
<td>Si1</td>
<td>0.0000</td>
<td>0.6743 (1)</td>
<td>0.3451 (4)</td>
<td>0.0071 (1)</td>
</tr>
<tr>
<td>S1</td>
<td>0.0000</td>
<td>0.3611 (1)</td>
<td>0.4632 (1)</td>
<td>0.0094 (1)</td>
</tr>
<tr>
<td>S2</td>
<td>0.0000</td>
<td>0.6784 (1)</td>
<td>0.9961 (2)</td>
<td>0.0089 (2)</td>
</tr>
<tr>
<td>S3</td>
<td>0.26269 (8)</td>
<td>0.1724 (1)</td>
<td>-0.0411 (1)</td>
<td>0.0100 (1)</td>
</tr>
</tbody>
</table>

**Table 2.5 Atomic displacement parameters (Å^2)**

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<tr>
<th></th>
<th>U^{11}</th>
<th>U^{22}</th>
<th>U^{33}</th>
<th>U^{12}</th>
<th>U^{13}</th>
<th>U^{23}</th>
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<tr>
<td>Cu1</td>
<td>0.0141 (1)</td>
<td>0.0135 (1)</td>
<td>0.0125 (2)</td>
<td>-0.0007 (1)</td>
<td>-0.0008 (1)</td>
<td>0.0000 (2)</td>
</tr>
<tr>
<td>Zn1</td>
<td>0.0235 (2)</td>
<td>0.0210 (2)</td>
<td>0.0191 (3)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-0.0016 (3)</td>
</tr>
<tr>
<td>Si1</td>
<td>0.0078 (3)</td>
<td>0.0077 (3)</td>
<td>0.0058 (5)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0007 (4)</td>
</tr>
<tr>
<td>S1</td>
<td>0.0126 (3)</td>
<td>0.0072 (3)</td>
<td>0.0085 (5)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0011 (4)</td>
</tr>
<tr>
<td>S2</td>
<td>0.0099 (3)</td>
<td>0.0104 (3)</td>
<td>0.0064 (6)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-0.0001 (3)</td>
</tr>
<tr>
<td>S3</td>
<td>0.0089 (2)</td>
<td>0.0101 (3)</td>
<td>0.0110 (5)</td>
<td>-0.0012 (1)</td>
<td>0.0006 (3)</td>
<td>0.0000 (3)</td>
</tr>
</tbody>
</table>
Table 2.6 Selected bond lengths (Å)

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Cu1—S2</th>
<th>Zn1—S3</th>
<th>Cu1—S3</th>
<th>Zn1—S3</th>
<th>Cu1—S1</th>
<th>Si1—S1</th>
<th>Zn1—S1</th>
<th>Si1—S2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.3170 (7)</td>
<td>2.3650 (7)</td>
<td>2.325 (1)</td>
<td>2.3650 (7)</td>
<td>2.3270 (6)</td>
<td>2.131 (1)</td>
<td>2.3426 (7)</td>
<td>2.136 (1)</td>
</tr>
<tr>
<td></td>
<td>2.325 (1)</td>
<td>2.3650 (7)</td>
<td>2.3270 (6)</td>
<td>2.131 (1)</td>
<td>2.322 (1)</td>
<td>2.136 (1)</td>
<td>2.322 (1)</td>
<td>2.143 (3)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x+1/2, -y+1, z-1/2; (ii) -x+1/2, -y, z+1/2; (iii) -x, y, z+1; (iv) x, y, z+1; (v) -x+1/2, -y+1, z+1/2; (vi) x-1/2, -y+1, z+1/2; (vii) x, y, z-1.

Data collection: SMART; cell refinement: SAINT; data reduction: SAINT; program(s) used to solve structure: SHELXS97; program(s) used to refine structure: SHELXL97; molecular graphics: CrystalMaker; software used to prepare material for publication: publCIF.

2.4 Conclusions

Single crystals of Cu₂ZnSiS₄, copper zinc silicon sulfide, have been prepared via high-temperature solid-state synthesis. The structure of Cu₂ZnSiS₄ has been solved and refined in the space group Pmn2₁. Cu₂ZnSiS₄ was found to have the wurtz-stannite structure type, like that of Li₂CdGeS₄, Li₂CdSnS₄, and Cu₂CdSiS₄. Each sulfur anion is tetrahedrally coordinated to 2 Cu cations, 1 Si cation, and 1 Zn cation, to form a three-dimensional, honeycomb structure. When viewed along the c axis, the atoms are aligned in rows where each cation alternates with the sulfur anions.

2.5 References

Reprinted from Acta Crystallographica, E67, Kimberly A. Rosmus, Jennifer A. Aitken,
Cu$_2$ZnSiS$_4$, i28, 2011.


3. Synchrotron X-ray Powder Diffraction and Electronic Band Structure of $\alpha$- and $\beta$-Cu$_2$ZnSiS$_4$

3.1 Introduction

Quaternary diamond-like semiconductors (DLSs) are materials that have structures derived from either cubic or hexagonal diamond. The increase in compositional flexibility, achieved by the greater number of cations and anions in the structure, allows for tuning the physical properties of the materials for various applications. DLSs with the formula I$_2$-II-IV-VI$_4$ exhibit technologically important physical and chemical properties, demonstrated by their potential in photovoltaics,$^{110-113}$ thermoelectrics,$^{114-116}$ and nonlinear optics.$^{117}$ For example, Mitzi and coworkers have fabricated a solar cell device comprised of a solid-solution of the earth-abundant Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSe) with an impressive 9.6% efficiency.$^{113}$ In the area of thermoelectrics, several substituted quaternary DLSs are competitive with clathrates and filled skutterudites at high temperature.$^{118-121}$ For example, heavily-doped CZTSe (Cu$_2$ZnSn$_{1-x}$In$_x$Se$_4$) has been found to have a thermoelectric figure of merit, ZT, of 0.95 at 850 K.$^{116}$ When investigating second harmonic generation, Li$_2$CdSnS$_4$ and Li$_2$CdGeS$_4$ were shown to have SHG responses of 100X and 70X $\alpha$-quartz, respectively.$^{117}$

The investigation of both the crystal and electronic structures of quaternary DLSs is essential in understanding the origin of the physicochemical properties and formulating structure-property and composition-property correlations. Using density functional theory (DFT) calculations, Chen et al. have predicted the ground state structures (at 0 K) for a number of I$_2$-II-IV-VI$_4$ DLSs.$^{122}$ They predict that these materials will have one of the following structures types: (i) kesterite (tetragonal I-4), (ii) stannite (tetragonal I-42m), (iii) wurtz-stannite (orthorhombic Pmn2$_1$), or (iv) wurtz-kesterite (monoclinic $P_c$).$^{122,123}$
For example, they predict a wurtz-kesterite structure for Ag$_2$ZnSiS$_4$ and Ag$_2$CdGeS$_4$, while for Cu$_2$ZnSiS$_4$ the kesterite structure is predicted to be most stable. Recently, single crystal X-ray diffraction has shown Ag$_2$ZnSiS$_4$ to crystallize in the space group $Pn$,\textsuperscript{124} in agreement with the ground-state calculation of Chen et al. On the other hand, experimental data show that Ag$_2$CdGeS$_4$\textsuperscript{125} possesses the Li$_2$CoSiO$_4$ structure-type,\textsuperscript{126} crystallizing in the space group $Pna2_1$, an option not considered in the study by Chen and coworkers. Experimentally, Cu$_2$ZnSiS$_4$ has only been shown to possess the wurtz-stannite structure ($Pmn2_1$) until now.\textsuperscript{127}-\textsuperscript{134}

Caution must be taken when studying the structure of Cu$_2$ZnSiS$_4$ since Cu$^+$ and Zn$^{2+}$ are isoelectronic and nearly indistinguishable by X-ray diffraction. Additionally, the powder diffraction patterns for many of the quaternary DLS structures are strikingly similar and difficult to discern with the use of laboratory X-ray diffraction. However, we have recently shown that synchrotron X-ray powder diffraction studies are suitable for discriminating between two similar diamond-like structures due to the utilization of a shorter wavelength, which leads to higher resolution data and the ability to better distinguish isoelectronic ions.\textsuperscript{125} Here, through Rietveld refinement of the synchrotron powder diffraction data the presence of two polymorphs of Cu$_2$ZnSiS$_4$ were found in the same sample. These results confirm the previously reported $Pmn2_1$ structure of $\alpha$-Cu$_2$ZnSiS$_4$ and identify a new polymorph, $\beta$-Cu$_2$ZnSiS$_4$ that crystallizes in the $Pn$ space group. Additionally, this work presents the electronic structure for both polymorphs as well as a special discussion on correlating the experimental absorption spectrum reported here and those previously reported by others\textsuperscript{128-134} to the calculated electronic structures.
3.2 Experimental

3.2.1 Reagents

Copper powder, 99.999%, Strem, Newburyport, MA; silicon powder, 99.999%, Strem, Newburyport, MA; sulfur powder, sublimed, 99.5%, Fisher Scientific, Pittsburgh, PA; zinc powder, 99.999%, Strem, Newburyport, MA

3.2.2 Synthesis

High-temperature solid-state synthesis was used to prepare $\alpha$- and $\beta$-Cu$_2$ZnSiS$_4$. In an argon-filled glovebox, stoichiometric ratios of the elements were weighed and ground in an agate mortar and pestle for 30 min. The sample was then transferred to a graphite crucible and inserted in a 12 mm outer diameter fused-silica tube. The tube was flame-sealed under a vacuum of $10^{-3}$ mbar using an oxy-methane torch. In a computer-controlled furnace, the sample was heated to 1000 °C over 12 hrs, held at 1000 °C for 96 hrs and then cooled at a rate of 7.5 °C to ambient temperature.

3.2.3 Synchrotron X-ray Powder Diffraction

High-resolution synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using an average wavelength of 0.413838 Å. Discrete detectors covering an angular range from -6 to 16° 2θ were scanned over a 34° 2θ range, with data points collected every 0.001° 2θ and a scan speed of 0.01°/s.

The 11-BM instrument uses X-ray optics with two platinum-stripped mirrors and a double-crystal Si(111) monochromator, where the second crystal has an adjustable sagittal bend. Ion chambers monitor incident flux. A vertical Huber 480 goniometer,
equipped with a eidenhain encoder, positions an analyzer system comprised of twelve perfect Si(111) analyzers and twelve Oxford-Danfysik LaCl$_3$ scintillators, with a spacing of 2° 2θ. The sample was spun during data collection. A Mitsubishi robotic arm was used to mount and dismount the sample on the diffractometer. Data were collected at room temperature, 180 K and 100 K. Low temperature was achieved by the use of an Oxford Cryosystems, Cryostream Plus device.

The diffractometer was controlled via EPICS. Data were collected while continually scanning the diffractometer 2θ arm. A mixture of NIST standard reference materials, Si (SRM 640c) and Al$_2$O$_3$ (SRM 676) was used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Corrections were applied for detector sensitivity, 2θ offset, small differences in wavelength between detectors, and the source intensity, as noted by the ion chamber before merging the data into a single set of intensities evenly spaced in 2θ.

Rietveld refinement was carried out with GSAS/EXPGUI. The starting model for $\alpha$-Cu$_2$ZnSiS$_4$ was obtained from the previously reported structure (Pmn2$_1$) obtained from single crystal X-ray diffraction. The structure of Li$_2$ZnSnS$_4$ (Pn) was used as the starting model for $\beta$-Cu$_2$ZnSiS$_4$. Rietveld refinement indicated the new polymorph, $\beta$-Cu$_2$ZnSiS$_4$, as the major phase (Table 3.1 and Table 3.2) while a small amount of the previously known $\alpha$-Cu$_2$ZnSiS$_4$ and extremely small quantities of several impurity phases were also present. The impurity phases, SiO$_2$, graphite, and an unidentified cubic phase in the space group $Fd-3m$, were modeled using the LeBail method within GSAS/EXPGUI due to the low quantity of impurity phases and the broad nature of their peaks. The few peaks resulting from these unwanted phases were found to
have little influence on the refinement of either Cu$_2$ZnSiS$_4$ phase; however, the omission of these phases from the refinement prevents an accurate model of the background leading to higher $\chi^2$ and wRp values.

The background was fitted with a shifted Chebyshev polynomial with 20 terms. All atoms were refined independently and isotropically for the duration of refinement with the exception of the isoelectronic Cu$^+$ and Zn$^{2+}$ ions, which were constrained to have equal isotropic displacement parameters until the final stage of the refinement. The peak shapes were accounted for through refinement of the Gaussian and Lorentzian terms; however, were better described by the Lorentzian influence due to the nature of this high-resolution data the peak shapes. The least squares for this refinement converged with $\chi^2 = 5.554$, Rp = 0.0857 (all data) and wRp = 0.1173 (all data).

### 3.2.4 Diffuse Reflectance UV/Vis/NIR

A Varian Cary 5000 spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory was used to collect the diffuse reflectance UV/Vis/NIR spectrum of the $\alpha$- and $\beta$-Cu$_2$ZnSiS$_4$. The sample was ground for 30 mins and placed in a sample holder. Barium sulfate was used as a 100% reflectance standard. The measurement was conducted at a scan rate of 600 nm/min. Using the Kubelka-Munk equation, the percent reflectance was converted to absorption, while the wavelength was converted to energy.

### 3.2.5 Computational methods

Electronic structure calculations, band structure and density of states (DOS), for both polymorphs of Cu$_2$ZnSiS$_4$, were performed using the WIEN2k computational software package (version 11.1). WIEN2k utilizes the full potential, linearized
augmented plane wave (LAPW) + local orbital method of density functional theory (DFT). DFT simplifies the many-body problem of interacting electrons and nuclei to a series of one-electron equations, the Kohn-Sham (KS) equations, which are solved using the LAPW method. More details about the WIEN2k calculations can be found in references 145, 146. The refined crystal structure of α-Cu₂ZnSiS₄ in the \( Pmn2_1 \) space group (from single crystal X-ray diffraction data) and β-Cu₂ZnSiS₄ in the \( Pn \) space group (from the Rietveld refinement of synchrotron powder diffraction data) were used to initialize the electronic structure calculations.¹²⁷ In these calculations, the muffin tin radii (RMT) of Cu, Zn, Si, and S were set to 2.23, 2.25, 1.93, and 1.97 bohr respectively. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) functional was used to treat exchange and correlation effects and a total of 1000 k-points in the full Brillouin zone were used.¹⁴⁷ Self-consistent calculations were considered to be converged when the change in total energy is less than 0.1 mRy/unit cell. The set of high symmetry points used for plotting the band structure in the irreducible Brillouin zone (IBZ) is an automatic (arbitrary) path, based on the template files of WIEN2k.

3.3 Results and discussions

High-resolution synchrotron X-ray powder diffraction was performed on a sample of Cu₂ZnSiS₄ to refine the structure of the material (Figure 3.1). The previously established model of Cu₂ZnSiS₄ in the wurtz-stannite structure (\( Pmn2_1 \)) was used as a starting model for this refinement. However, the data clearly shows additional distinct peaks flanking the expected peaks, which indicate wurtz-stannite is not the only phase present (Figure 3.2). The additional peaks were accounted for after adding the wurtz-kesterite phase (\( Pn \)) of Cu₂ZnSiS₄ to the refinement (Table 3.1). The wurtz-kesterite
structure was considered due to its extreme similarity to the wurtz-stannite structure, compounded by the isoelectronic nature of the Cu$^+$ and the Zn$^{2+}$ ions. It was determined that the collected data could only be modeled using both phases, leading to the conclusion that there are two polymorphs of the compound, $\alpha$-Cu$_2$ZnSiS$_4$ ($Pmn2_1$) and $\beta$-Cu$_2$ZnSiS$_4$ ($Pn$). To completely account for all of the observed data, three impurity phases were added to the refinement, SiO$_2$, graphite, and an unknown phase in the cubic space group $Fd-3m$. The SiO$_2$ and the graphite are believed to come from the reaction vessels used to synthesize the material. The peaks of these phases have nearly no overlap with the main peaks from either Cu$_2$ZnSiS$_4$ phase.

Figure 3.1. The Rietveld refinement of the two polymorphs of Cu$_2$ZnSiS$_4$ using synchrotron X-ray powder diffraction. The observed data (+) is fitted with the calculated data (solid line). Underneath the data are three rows of tick marks (\|) which indicate the locations of the calculated peaks of the $Pn$ space group, the $Pmn2_1$ space group, and of the impurities. Below is the difference plot (solid line).
Figure 3.2. A comparison of selected peaks of the collected synchrotron data (solid black line) to the calculated patterns of Cu$_2$ZnSiS$_4$ in the space groups $Pn$ (blue dashed line) and $Pmn2_1$ (red dotted line).

Table 3.1. Results from the using the synchrotron X-ray powder diffraction data for $\beta$-Cu$_2$ZnSiS$_4$ that was refined using GSAS/EXPGUI.

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>$\beta$-Cu$_2$ZnSiS$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>697.596</td>
</tr>
<tr>
<td>Temperature</td>
<td>180 K</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>11-BM</td>
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<tr>
<td>Wavelength</td>
<td>0.4130460 Å</td>
</tr>
<tr>
<td>Space group</td>
<td>$Pn$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 6.134092(6) Å</td>
</tr>
<tr>
<td></td>
<td>b = 6.392752(5) Å</td>
</tr>
<tr>
<td></td>
<td>c = 7.421228(8) Å</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \gamma = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 90.056(1)^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>291.014(1) Å$^3$</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>Calculated density</td>
<td>3.981 Mg m$^{-3}$</td>
</tr>
<tr>
<td>20 range</td>
<td>0.5 to 50</td>
</tr>
<tr>
<td>Refinement mode</td>
<td>Full profile Rietveld</td>
</tr>
<tr>
<td>Goodness of Fit</td>
<td>$\chi^2 = 5.554$</td>
</tr>
<tr>
<td>$R_p$, $wR_p$</td>
<td>$R_p = 0.0857$, $wR_p = 0.1173$</td>
</tr>
</tbody>
</table>
β-Cu$_2$ZnSiS$_4$ crystallizes in the monoclinic space group $Pn$ with 8 atoms located on general positions (Figure 3.3, Table 3.2). The S$^{2-}$ anions make up a hexagonal closest packed array where the Cu$^+$, Zn$^{2+}$, and Si$^{4+}$ reside in half of the tetrahedral holes. Each sulfide anion is surrounded by two Cu$^+$ ions, one Zn$^{2+}$ ion, and one Si$^{4+}$ ion. All tetrahedra in the structure are very regular with an average bond angle of 109.5°. The average Cu-S and Zn-S bond distances are nearly identical. However, the Cu-S bond distance range is approximately 0.02 Å and 0.05 Å greater for Cu(1) and Cu(2) respectively, than the Zn-S range. The bond distances and angles in β-Cu$_2$ZnSiS$_4$ are comparable to those found in the α-phase with the exception of the Cu(2) site, which has a greater variance in bond distances.

![Figure 3.3. β-Cu$_2$ZnSiS$_4$ viewed along the a-axis showing a three-dimensional honeycomb structure.](image)
Table 3.2. Fractional atomic coordinates and equivalent isotropic displacement parameters for β-Cu₂ZnSiS₄.

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso (Å²x10⁴)</th>
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<tbody>
<tr>
<td>Cu(1)</td>
<td>0.9207(2)</td>
<td>0.6731(4)</td>
<td>0.2767(2)</td>
<td>67(4)</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>0.4159(2)</td>
<td>0.8480(1)</td>
<td>0.5256(3)</td>
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<tr>
<td>Zn(1)</td>
<td>0.9170(2)</td>
<td>0.6754(4)</td>
<td>0.7709(2)</td>
<td>75(4)</td>
</tr>
<tr>
<td>Si(1)</td>
<td>0.9163(5)</td>
<td>1.1744(2)</td>
<td>0.5245(7)</td>
<td>69(4)</td>
</tr>
<tr>
<td>S(1)</td>
<td>0.2970(4)</td>
<td>0.6726(6)</td>
<td>0.7873(2)</td>
<td>46(1)</td>
</tr>
<tr>
<td>S(2)</td>
<td>0.2964(4)</td>
<td>0.6725(6)</td>
<td>0.2605(2)</td>
<td>47(1)</td>
</tr>
<tr>
<td>S(3)</td>
<td>0.2633(2)</td>
<td>1.1779(2)</td>
<td>0.5272(4)</td>
<td>46(1)</td>
</tr>
<tr>
<td>S(4)</td>
<td>0.7915(2)</td>
<td>0.8619(2)</td>
<td>0.5229(4)</td>
<td>51(1)</td>
</tr>
</tbody>
</table>

The two polymorphs of Cu₂ZnSiS₄ differ only in the cation ordering of the Cu⁺ and Zn²⁺ sites; each structure has an identical array of SiS₄ tetrahedra (Figure 3.4). In both structures, all of the cations are aligned in rows along the b-axis. In the β-phase along the a-axis there are alternating columns of Cu(1)-Si-Cu(1) with Zn-Cu(2)-Zn tetrahedra. Along the equivalent axis in the α-phase (c-axis), there exist columns of alternating Zn-Si-Zn and Cu(1) tetrahedra.

Figure 3.4. Polyhedral view along the b-axis for the α-Cu₂ZnSiS₄ (top) and β-Cu₂ZnSiS₄ (bottom).
The calculated electronic band structure and DOS of both $\alpha$-Cu$_2$ZnSiS$_4$ and $\beta$-Cu$_2$ZnSiS$_4$ are shown in Figures 3.5-3.8. The total energy was calculated to be -27972.64989 Ry and -27972.65612 Ry for $\alpha$-Cu$_2$ZnSiS$_4$ and $\beta$-Cu$_2$ZnSiS$_4$, respectively. The energy difference between the two structures is 0.08476 eV. Although neither of these polymorphs have the kesterite structure, which is predicted by Chen et al. to be the ground state structure for Cu$_2$ZnSiS$_4$, the relative energies of the two polymorphs are in accordance with that calculated by Chen and coworkers. As shown in Figures 3.5 and 3.6, both polymorphs of Cu$_2$ZnSiS$_4$ exhibit a direct band gap as evidenced by the valence band maximum (VBMax) and the conduction band minimum (CBMin) existing at the $\Gamma$-point of the irreducible Brillouin zone (IBZ). The calculated band gap energy ($E_g$) for $\alpha$-Cu$_2$ZnSiS$_4$ is 1.3 eV while that of $\beta$-Cu$_2$ZnSiS$_4$ is 1.7 eV. These calculated values are lower than the experimentally determined band gaps that are greater than 3.0 eV. The under-estimation of $E_g$ by DFT calculations using the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) functional is well known.

Figure 3.5. Band structure diagram of $\alpha$-Cu$_2$ZnSiS$_4$. The horizontal, dashed line denotes the Fermi level ($E_F$).
Figure 3.6. Band structure diagram of $\beta$-Cu$_2$ZnSiS$_4$. The horizontal, dashed line denotes the Fermi level ($E_F$).

The total and partial DOS for $\alpha$-Cu$_2$ZnSiS$_4$ is shown in Figure 3.7. The total DOS in the energy interval of -10 to 10 eV is comprised of contributions from a copper atom, a zinc atom, a silicon atom, and three crystallographically unique sulfur atoms. The core bands in the energy range of -10 to -6.5 eV have major contributions from the Zn-$d$ and Si-$s$ orbitals. In the energy range of -6.5 to 0 eV, the major contributions are from the Cu-$d$ and the S-$p$ orbitals. As is the case with the Cu-III-VI$_2$ chalcopyrite DLSs and the wurtz-kesterite-type Ag$_2$ZnSiS$_4$, the VBMax in the wurtz-stannite-type Cu$_2$ZnSiS$_4$ is dominated by the hybridization of the Cu/Ag-$d$ and chalcogen-$p$ states.$^{124,149}$ The most significant contributions to the CBMin from the range of 1.3 to 5 eV are from the Zn-$s$, Si-$s$, Si-$p$ and S-$p$ orbitals. It should be noted that the Si-$s$ and Si-$p$ contributions are similar in the lowest region of the CBMin while the Si-$p$ has greater contributions after 3 eV. The composition of the CBMin in this structure is similar to that of Ag$_2$ZnSiS$_4$ except that the Si-$s$ has greater contribution than Si-$p$ at the lowest CBMin energies for the silver analog.
Figure 3.7. Density of states diagram of $\alpha$-Cu$_2$ZnSiS$_4$ The vertical, solid line denotes the Fermi level ($E_F$).

While the overall DOS for $\beta$-Cu$_2$ZnSiS$_4$ is strikingly similar to that of $\alpha$-Cu$_2$ZnSiS$_4$, there exist some subtle differences (Figure 3.8). Although the atomic identity of the major contributors in each region is the same, the magnitude of states per eV are noticeably different for the two structures. Another minor difference is that the contributions from each of the four crystallographically unique sulfur atoms near the VBMax in the $\beta$-phase are nearly identical; however, these contributions are less evenly distributed among the three unique sulfur atoms in the $\alpha$-phase. Additionally, there are also differences in the partial DOS for silicon. In the $\beta$-phase the lowest CBMin is almost entirely comprised of Si-$s$ states, followed by a region of equal contributions from Si-$s$ and Si-$p$, and lastly a higher energy region that is mainly Si-$p$ in character.
Figure 3.8. Density of states diagram of $\beta$-Cu$_2$ZnSiS$_4$. The vertical, solid line denotes the Fermi level ($E_F$).

The optical diffuse reflectance spectrum for Cu$_2$ZnSiS$_4$ was obtained on a powdered sample, Figure 3.9. The majority of the optical absorption edge seems to be indicative of a single phase material; however, a small tail is apparent on the lower energy side of the absorption edge upon careful examination. The electronic band structure calculations show that the band gap of the $\beta$-phase should be higher in energy than that of the $\alpha$-phase. Although the calculated band gaps are severely underestimated, the relative energies of the two phases should be comparable. Based on this information we can tentatively assign a band gap of $\sim 3.2$ eV to the $\beta$-phase and a band gap, $\sim 3.0$ eV to that of the $\alpha$-phase. The shape of the absorption edge is also in agreement with the results of the Rietveld refinement of the synchrotron powder diffraction data, which indicates that the $\beta$-phase is present in a much greater amount than the $\alpha$-phase.

The band gap of Cu$_2$ZnSiS$_4$ was reported by Wold and coworkers in 1977 as 3.25 eV; and later in 1987, the same group reported the band gap as 3.04 eV. 128,129 Upon
examining the absorption spectrum published in the 1977 paper, one can see the clear presence of a significant absorption edge tail at lower energy.\textsuperscript{128} This spectrum is similar to that which we report here and have assigned as resulting from a mixture of both α- and β-Cu\textsubscript{2}ZnSiS\textsubscript{4}.

![Absorption Spectrum](Image)

**Figure 3.9. The experimental band gap of Cu\textsubscript{2}ZnSiS\textsubscript{4}.

In more recent works by Levcenco et al., several band gaps ranging from 2.97 to 3.41 eV were reported for Cu\textsubscript{2}ZnSiS\textsubscript{4} using polarization-dependent piezoreflectance (PzR),\textsuperscript{131} surface photovoltage (SPV) spectroscopy,\textsuperscript{132,133} and electrolyte electroreflectance (EER) measurements.\textsuperscript{134} It is interesting to note that while our measurement was performed on a powdered sample, Levcenco and Wold’s groups prepared their samples as crystals using the iodine vapor transport method. Although each group reported their material as possessing the wurtz-stannite structure, it is quite possible that the crystals could have been an intergrowth of the α- and β-phases.
However, the diffraction methods that were used in both of these studies did not have the ability to indicate the presence of two phases since their peaks could not be resolved.

Further ambiguity in the interpretation of the optical spectra arises from the fact that, in addition to the presence of two polymorphs, there exist other accessible transitions within the band structure of each phase at the Γ-point. As shown in Figure 3.10, there exist four bands at the Γ-point whose energies differ by ~250 meV for α- and β-Cu₂ZnSiS₄. The close spacing of these bands near the VBMₐx allows for the possibility of multiple electronic excitations that can be observed for the material. The observation of multiple bands with similar energies near the band gap has also been observed for CZTS and CZTSe, as calculated by Persson using the LAPW method of DFT.¹⁵⁰ Likewise, Chen and coworkers have proposed similar excitonic transitions for I-III-II₂-VI₄ and II-III-IV-V₄ diamond-like materials.

Figure 3.10. Expanded view of the calculated electronic band structure showing the accessible transitions for α-Cu₂ZnSiS₄ (top) and β-Cu₂ZnSiS₄ (bottom).
3.4 Conclusions

A sample of Cu$_2$ZnSiS$_4$ was characterized using high-resolution synchrotron powder diffraction. The refinement of this data confirmed the previously reported structure for Cu$_2$ZnSiS$_4$ in $Pmnm$ and identified a new polymorph, β-Cu$_2$ZnSiS$_4$, crystallizing in the space group $Pn$. Electronic structure calculations using WIEN2k showed direct band gaps of 1.3 and 1.7 eV for the $\alpha$- and $\beta$-phases respectively. The VBMax was found to be dominated by the Cu-$d$ and S-$p$ orbitals, similar to the chalcopyrite type DLSs. Electronic structure calculations and the Rietvled refinement results help to explain the observed optical absorption spectrum observed for Cu$_2$ZnSiS$_4$, which shows multiple absorption edges, from which we estimate band gaps of 3.2 and 3.0 eV for the $\beta$- and $\alpha$-phases respectively. Synthesis of each polymorph as a pure-phase material is challenging due to their similar relative energies, yet this is imperative for the further physicochemical characterization of both polymorphs.

3.5 References

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4. Optical Nonlinearity in Cu₂CdSnS₄ and α/β-Cu₂ZnSiS₄, Diamond-like Semiconductors with High Laser-Damage Thresholds

4.1 Introduction

Improved nonlinear optical (NLO) materials for applications in the infrared (IR) region are essential to advancing telecommunications, biomedical imaging, and diagnostics, such as the detection of trace gases. Some of the criteria for ideal NLO materials are: noncentrosymmetric (NCS) structure, high optical nonlinearity, extreme optical transparency, environmental stability, large laser-damage threshold (LDT), and high thermal stability. Considering this long list, the quest for “ideal” NLO materials proves challenging. While there are several attractive NLO crystals for use in the visible and near-IR regions, there are fewer options for use further in the IR and no one material offers radiation in the entire region.

While several NLO crystals are useful for generation in the mid-IR, each suffers drawbacks. For operating a 2 μm-pumped optical parametric oscillator at wavelengths between 2-8 μm, ZnGeP₂ is used because it is transparent and phase matchable (PM) at 2 μm and has a large χ(2) of 150 pm/V, yet is limited at longer wavelengths due to multiple photon absorption. Therefore, in the region of ~9-11 μm, AgGaSe₂ is the material of choice for wavelength (λ) conversion; however, it is plagued by two-photon absorption (2PA) and has inadequate birefringence for 1 μm phase matching. AgGaS₂ is PM at 1 μm with a χ(2) of 36 pm/V; but, it has a low LDT due to 2PA.

Some new materials show potential in IR NLO applications. For example, Ba₈Sn₄S₁₅ has wide optical transparency, a χ(2) of 23.92 pm/V and a LDT that is ~26× AgGaS₂ when irradiated with a 1.064 μm laser; but, it is non-phase matchable (NPM) at 2.05 μm. NaAsSe₂ shows strong second harmonic generation (SHG), but is NPM at
1.58 μm. The ACd\textsubscript{4}In\textsubscript{5}Se\textsubscript{12} (A=Rb, Cs) compounds exhibit wide optical transparency ranges and excellent SHG responses, ~35-40× AgGaS\textsubscript{2} at 2.05 μm, but are also NPM at 2.05 μm. Practical applications require improved materials that are accessible by robust design.

Since the discovery of new compounds for SHG applications is contingent on NCS crystal structures, many strategies utilize exploratory synthesis involving acentric building units. This approach, although appealing for unexpected and interesting structures, is a gamble for finding NCS materials since acentric building units often pack into centrosymmetric structures. In contrast, diamond-like semiconductors (DLSs) provide a reliable route to attractive SHG materials, as the compositions are predictable and the structures are inherently NCS since the MS\textsubscript{4} tetrahedra align in one direction. Additionally, DLSs provide chemical flexibility that can be exploited to tune properties, such as phase matching and refractive index. High optical nonlinearity arises in these materials as a consequence of the predominately covalent bonding. Indeed, DLSs dominate the list of commercially available materials, such as AgGaS\textsubscript{2}, AgGaSe\textsubscript{2}, and ZnGeP\textsubscript{2}.

In 1981, Pamplin predicted compositions of multinary DLSs and stated “there are a thousand adamantine [diamond-like] phases from which to choose device material. [The] crystal growth and characterization should continue in as many laboratories as possible.” Here, using Cu\textsubscript{2}CdSnS\textsubscript{4} and α/β-Cu\textsubscript{2}ZnSiS\textsubscript{4}, we demonstrate how a change from Sn to Si for the IV ion in the I\textsubscript{2}-II-IV-VI\textsubscript{4} formula can have significant effects on key characteristics critical for NLO applications. Establishing structure-property correlations is imperative for directing efforts towards the most promising...
materials.

4.2 Experimental

4.2.1 Reagents

Copper powder, 99.999%, Strem, Newburyport, MA; cadmium powder, 99.999%, Strem Newburyport, MA; silicon powder, 99.999%, Strem, Newburyport, MA; sulfur powder, sublimed, 99.5%, Fisher Scientific, Pittsburgh, PA; tin powder, 99.999%, Strem, Newburyport, MA; zinc powder, 99.999%, Strem, Newburyport, MA.

4.2.2 Synthesis

Cu₂CdSnS₄ and α/β-Cu₂ZnSiS₄ were prepared via high-temperature solid-state synthesis. The starting materials were weighed in stoichiometric amounts, where 1 mmol was used as 1 equivalent, and ground in an agate mortar and pestle for 30 min in an argon-filled glove box. Each sample was placed into a graphite crucible, which was then inserted into a 12 mm outer diameter fused-silica tube. The tube was flamed-sealed under a vacuum of 10⁻³ mbar using an oxy-methane torch. The samples of Cu₂CdSnS₄ were heated to 800 °C over 12 h and held at that temperature for 125 h. The samples were then cooled to 500 °C over 50 h, at a rate of 6 °C/hr and then cooled to ambient temperature. The heating profile for α/β-Cu₂ZnSiS₄ can be found in Rosmus et al.¹⁶¹

4.2.3 Single Crystal Diffraction

A Bruker SMART Apex II CCD single crystal X-ray diffractometer employing graphite monochromatized molybdenum Kα radiation with a wavelength of 0.71073 Å and operating with a tube power of 50 kV and 30 mA was used to collect the data for 40 s/frame at ambient temperature. A total of 2930 measured reflections was collected with
293 of them unique. The program SAINT\textsuperscript{162} was used to integrate the data and SADABS\textsuperscript{163} was employed to perform the absorption correction. XPREP was used for space group determination and to create files for SHELXTL. Based on systematic absences, I-4 (#82), I4/m (#87), I4 (#79), I-42m (#121), I4/mmm (#139), I-4m2 (#119), I422 (#97) and I4mm (#107) were suggested space groups for Cu\textsubscript{2}CdSnS\textsubscript{4}. Because diamond structures are inherently noncentrosymmetric and there exist diamond-like materials crystallizing in I-4 and I-42m, these space groups were further considered. Since the data clearly showed systematic absences for hkl: l=2n, the space group I-42m was selected. The structure was solved using direct methods. Four atoms were located in special positions. Results can be found in Table 4.1 and the deposited crystallographic information file (cif).

Table 4.1. Results from single crystal X-ray diffraction data for Cu\textsubscript{2}CdSnS\textsubscript{4}.

<table>
<thead>
<tr>
<th>Space group</th>
<th>I-42m (No.121)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal size</td>
<td>0.06 mm x 0.05 mm x 0.03 mm</td>
</tr>
<tr>
<td>Formula weight</td>
<td>486.41 g mol\textsuperscript{-1}</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 5.592 (1) Å</td>
</tr>
<tr>
<td></td>
<td>b = 5.592 (1) Å</td>
</tr>
<tr>
<td></td>
<td>c = 10.840 (2) Å</td>
</tr>
<tr>
<td>Volume</td>
<td>338.969 (1) Å\textsuperscript{3}</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Calculated density</td>
<td>4.766 Mg/m\textsuperscript{3}</td>
</tr>
<tr>
<td>Reflections collected/unique</td>
<td>2930/293</td>
</tr>
<tr>
<td>Data/Restrains/Parameters</td>
<td>293/0/14</td>
</tr>
<tr>
<td>Completeness to θ=27.51</td>
<td>100%</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>0.04(3)</td>
</tr>
<tr>
<td>F(000)</td>
<td>440</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1=0.0090, wR2=0.0196</td>
</tr>
<tr>
<td>Final R indices (all data)</td>
<td>R1=0.0086, wR2=0.0193</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.16</td>
</tr>
<tr>
<td>Largest peak</td>
<td>0.90 e\textsuperscript{-}\textsuperscript{Å\textsuperscript{3}}</td>
</tr>
<tr>
<td>Deepest hole</td>
<td>-0.368 e\textsuperscript{-}\textsuperscript{Å\textsuperscript{3}}</td>
</tr>
</tbody>
</table>

Refinement of F\textsuperscript{2} was made against all reflections.

\[ R_1 = (\sum |F_o|-|F_c|)\sqrt{(\sum |F_o|)} \]
\[ wR_2 = \sqrt{\sum w(F_o^2-F_c^2)^2}/\sum (w(F_o^2))^2] \]
\[ w = 1/(\sigma^2(F_o^2)+aF_o^2+bP) \]
\[ P = [2F_c^2+Max(F_o^2,0)]/3 \]
4.2.4 High Resolution Synchrotron X-ray Powder Diffraction

High-resolution synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using an average wavelength of 0.413838 Å for powdered samples of α/β-Cu$_2$ZnSiS$_4$ as well as Cu$_2$CdSnS$_4$, which was ground with silicon standard. Discrete detectors covering an angular range from -6 to 16° 2θ were scanned over a 34° 2θ range, with data points collected every 0.001° 2θ and a scan speed of 0.01°/s. The 11-BM instrument uses X-ray optics with two platinum-stripped mirrors and a double-crystal Si(111) monochromator, where the second crystal has an adjustable sagittal bend. Ion chambers monitor incident flux. A vertical Huber 480 goniometer, equipped with a Heidenhain encoder, positions an analyzer system comprised of twelve perfect Si(111) analyzers and twelve Oxford-Danfysik LaCl$_3$ scintillators, with a spacing of 2° 2θ. The sample was spun during data collection. A Mitsubishi robotic arm was used to mount and dismount the sample on the diffractometer. Data were collected at room temperature.

The diffractometer was controlled via EPICS and data were collected while continually scanning the diffractometer 2θ arm. A mixture of NIST standard reference materials, Si (SRM 640c) and Al$_2$O$_3$ (SRM 676) was used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Corrections were applied for detector sensitivity, 2θ offset, small differences in wavelength between detectors, and the source intensity, as noted by the ion chamber before merging the data into a single set of intensities evenly spaced in 2θ. Rietveld refinements were carried out with GSAS/EXPGUI.
The single crystal structure determined in this work was used as the starting model for Cu$_2$CdSnS$_4$. There was one peak of very low intensity that could not be identified. This peak was not even discernable via laboratory X-ray powder diffraction. Final statistics were excellent even while not accounting for this peak due to its extremely weak intensity. The background was fitted with a shifted Chebyshev polynomial with 18 terms. The peak shapes were accounted for through refinement of the Lorentzian terms within the type-3 profile. Lattice parameters, atomic coordinates, and isotropic displacement parameters were refined. The least squares for this refinement converged with $\chi^2 = 1.882$, $R_p = 0.1129$ (all data) and $R_{wp} = 0.1331$ (all data), Figure 5.1.

The starting models for $\alpha$-Cu$_2$ZnSiS$_4$ and $\beta$-Cu$_2$ZnSiS$_4$ were obtained from our previous work. Additionally, ZnS was added to the starting model to account for a small impurity. Moreover, there were several very weak peaks, only observable by synchrotron diffraction, that were unable to be identified. Because they were so weak, not accounting for them had little effect on the overall statistics, which were deemed excellent. The background was fitted with a shifted Chebyshev polynomial with 18 terms. The peak shapes were accounted for through refinement of the Lorentzian terms within the type-3 profile. Lattice parameters, atomic coordinates, and isotropic displacement parameters were refined. The weight fractions for $\alpha$-Cu$_2$ZnSiS$_4$, $\beta$-Cu$_2$ZnSiS$_4$, ZnS were found to be 59(1)%, 40(1)%, and 0.3(1)%, respectively. The final refinement converged with $\chi^2 = 2.216$, $R_p = 0.0807$ (all data) and $R_{wp} = 0.0975$ (all data), Figure 4.1.
Figure 4.1. The Rietveld refinement results of Cu$_2$CdSnS$_4$ (left) and α/β-Cu$_2$ZnSiS$_4$ (right) using high-resolution synchrotron powder diffraction data. In each plot, the observed data (+) and the calculated data (red solid line) are shown at the top. Below the data for Cu$_2$CdSnS$_4$ are two rows of tick marks (ǀ) corresponding to the locations of the expected Bragg reflections of Si and Cu$_2$CdSnS$_4$, from top to bottom. Below the data for α/β-Cu$_2$ZnSiS$_4$ are three rows of tick marks (ǀ) corresponding to the locations of the expected Bragg reflections for α-Cu$_2$ZnSiS$_4$, β-Cu$_2$ZnSiS$_4$, and ZnS, from top to bottom. The difference between the observed and the calculated patterns (blue solid line) is shown at the bottom of each plot.

4.2.5 Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDS)

Semi-quantitative elemental analysis for Cu$_2$CdSnS$_4$ and α/β-Cu$_2$ZnSiS$_4$ (Figure 6.2) was executed using a Hitachi S-3400N scanning electron microscope equipped with a Bruker Quantax model 400 energy dispersive spectrometer using an XFlash® 5010 EDS detector with a 129 eV resolution. Small crystals of Cu$_2$CdSiS$_4$ and α/β-Cu$_2$ZnSiS$_4$ were attached to double-sided carbon tape that was adhered onto an aluminum specimen holder. EDS spectra were collected for three areas on each of three crystals for both
specimens at an accelerating voltage of 15 kV for 5 min live time at a working distance of 10 mm.

![ Representative EDS spectra of Cu$_2$CdSnS$_4$ (left) and α/β-Cu$_2$ZnSiS$_4$ (right).](image)

Figure 4.2. Representative EDS spectra of Cu$_2$CdSnS$_4$ (left) and α/β-Cu$_2$ZnSiS$_4$ (right).

When determining the composition of each compound, the oxygen and carbon from the carbon tape and the aluminum from the specimen holder were subtracted to acquire a composition based only on the elements within the crystals. The compositions were found to be Cu$_{2.2}$Cd$_{1.0}$Sn$_{1.0}$S$_{3.9}$ and Cu$_{2.1}$Zn$_{1.0}$Si$_{0.9}$S$_{3.5}$, which are close to the nominal compositions.

4.2.6 Differential Thermal Analysis

A Shimadzu DTA-50 thermal analyzer was employed for thermal analysis studies of Cu$_2$CdSnS$_4$ and α/β-Cu$_2$ZnSiS$_4$. A three-point calibration curve using the melting points of indium, zinc and gold metals was used to calibrate the instrument. The samples and an Al$_2$O$_3$ reference material of similar mass were sealed under vacuum in carbon-coated, fused-silica ampoules. The temperature was programmed to increase at a rate of 10 °C/min to 1000 °C, held for 1 min, and then cooled at 10 °C/min. Two cycles were performed in order to distinguish reversible and irreversible events (Figure 4.3).
Figure 4.3. Differential thermal analysis diagrams of the first heating/cooling cycle for (a) Cu₂CdSnS₄ and (c) α/β-Cu₂ZnSiS₄. The second cycle for (b) Cu₂CdSnS₄ and (d) α/β-Cu₂ZnSiS₄. The heating cycles are shown by the red dashed curves and the cooling cycles are depicted as blue solid curves. (e) Observed and calculated XRPD patterns for the DTA residue for Cu₂CdSnS₄.

The Cu₂CdSnS₄ sample exhibited one reversible event during heating and one during cooling. Each heating cycle showed an endothermic event at approximately 930°C.
that can be attributed to the melting point of the product, which is consistent with the melting point (926 °C) found by Matsushita et al. Each cooling cycle demonstrated an exothermic event, which is due to the recrystallization of the material at approximately 900°C. The DTA diagram of α/β-Cu2ZnSiS4 indicates no thermal events during the heating or the cooling cycles. This suggests that the melting point of the material is greater than 1000°C. Multiple measurements using different samples of α/β-Cu2ZnSiS4 were performed yielding the same results. The impurity, ZnS, has a melting point around 1700 °C. The DTA residues were analyzed using XRPD. The XRPD pattern for the residue of Cu2CdSnS4 matches well to the calculated and shows no additional phases, thus the material melts congruently. It is not possible to definitively determine if α/β-Cu2ZnSiS4 melts congruently or incongruently since the sample that went into the DTA tube already contained a small amount of ZnS.

4.2.7 Optical Diffuse Reflectance UV/VIS/NIR Spectroscopy

A Varian Cary 5000 spectrometer, equipped with a Harrick Praying Mantis diffuse reflectance accessory, was used to collect the optical diffuse reflectance spectra of Cu2CdSnS4 and α/β-Cu2ZnSiS4 over the ultraviolet, visible, and near infrared (UV/VIS/NIR) spectral regimes. Each sample was ground and a small amount was placed onto a compacted barium sulfate powder that was preloaded into the sample holder with a depth of 3 mm. Barium sulfate (Fisher, 99.92%) was used as a 100% reflectance standard. The measurement was conducted at a scan rate of 600 nm/min. For Cu2CdSnS4, the data were treated using the Kubelka-Munk transformation, \( \alpha_{KM} / s = (1-R)^2/(2R) \) and the raw reflectance (R) was converted to a relative absorption (α) since the scattering coefficient, s, is unknown. The Urbach energy was also obtained by fitting
the optical data to the functional form $\alpha = A \cdot \exp\left(\frac{E - E_g}{E_u}\right)$, where $A$ is a constant, $E$ is the photon energy in eV, $E_g$ is the bandgap energy, and $E_u$ is the Urbach energy.\textsuperscript{175} The bandgaps of $\alpha/\beta$-Cu$_2$ZnSiS$_4$ were roughly estimated by extrapolation of the absorption edge to the baseline as more careful treatment proved difficult since the sample was not a pure material but rather consisted of 59(1)% $\alpha$-Cu$_2$ZnSiS$_4$, 40(1)% $\beta$-Cu$_2$ZnSiS$_4$, and 0.3(1)% ZnS.

Figure 4.4. Relative Kubelka-Munk absorption of Cu$_2$CdSnS$_4$ derived from the optical diffuse reflectance UV/VIS/NIR spectrum; (a) log of the absorption as a function of energy with an overlaid fit used to determine the Urbach energy ($E_u$), (b) the square of the absorption as a function of energy (direct bandgap function), where the lighter region shows the linear portion of the curve, (c) the square root of the absorption as a function of energy (indirect bandgap function), where the lighter region shows the linear portion of the curve, and (d) relative absorption as a function of energy where the dotted curve shows the fitting used to estimate the bandgap energy ($E_g$).
The bandgap, the nature of the gap, and the Urbach tail energy were determined for Cu$_2$CdSnS$_4$ via optical diffuse reflectance UV/VIS/NIR spectroscopy data. The Urbach tail arises from impurities and defects within a compound, which essentially smears the top of the valence bands and the bottom of the conduction bands. The Urbach tail can be assigned by finding the linear portion of the data when plotting the logarithm (log) of the absorption as a function of photon energy. The fitting of the slope is the Urbach energy, which was found to be 0.1267(1) eV, Figure 4.4a. In determining the nature of the bandgap, whether direct (sharp absorption edge) or indirect (gradual onset of absorption edge), the absorption data were fitted to the function for a direct gap semiconductor, $\alpha = A \cdot (E - E_g)^{1/2} / E$ (Figure 4.4b), and to the function for an indirect semiconductor, $\alpha = A \cdot (E - E_g)^2 / E$ (Figure 4.4c), where $A$ is a constant, $E$ is the photon energy in eV, and $E_g$ is the bandgap energy. The data for Cu$_2$CdSnS$_4$ were better fit with the indirect function suggesting that it is an indirect bandgap semiconductor with a bandgap energy of 0.92 eV (Figure 4.4d). However, we cannot exclude a direct-gap case, in which the optical transition is extrinsically broadened by a significant Urbach tailing effect. Our band structure calculations indicate that Cu$_2$CdSnS$_4$ has a direct bandgap as detailed in Section 1.10; however, it should be noted that the calculations are performed for $T = 0$ K.

The bandgaps of $\alpha$-Cu$_2$ZnSiS$_4$ and $\beta$-Cu$_2$ZnSiS$_4$ have been previously reported as $\sim3.0$ and $\sim3.2$ eV.\(^1\) It is difficult to assign precise values to the bandgaps of $\alpha$-Cu$_2$ZnSiS$_4$ and $\beta$-Cu$_2$ZnSiS$_4$ because they are currently prepared as a mixture. Syntheses of pure phases are extremely challenging, due to the very similar ground state energies calculated for the two polymorphs.
4.2.8 Infrared Spectroscopy

Infrared spectroscopy was carried out using a Thermo Nicolet Nexus 470 FT-IR spectrometer. An ATR attachment with a germanium window was used to collect data from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). The data collection software OMNIC was used to collect 64 scans for Cu\(_2\)CdSnS\(_4\) and α/β-Cu\(_2\)ZnSiS\(_4\).

4.2.9 Nonlinear Optical (NLO) Properties

A summary of all nonlinear optical data is listed in Table 4.2.

4.2.9.1 Sample Preparation

Polycrystalline Cu\(_2\)CdSnS\(_4\) and a mixture of α/β-Cu\(_2\)ZnSiS\(_4\) were sieved into discrete particle size ranges of 0-20 μm, 20-45 μm, 45-63 μm, 63-75 μm, 75-90 μm, and 90-106 μm, in order to assess phase-matching behavior of the samples. In addition, α/β-Cu\(_2\)ZnSiS\(_4\) was also sieved into particle size ranges of 106-125 μm and 125-150 μm. Although the samples appear to be air stable, they were placed into fused-silica capillary tubes that were flame-sealed under vacuum to prevent exposure to air and moisture during the measurements. Each tube was loaded into a homemade sample holder that was mounted on a Z-scan translation stage. The microcrystalline AgGaSe\(_2\) (MC), a reference material, was prepared by Brant et al.\(^{176}\) In addition, a comparison between the microcrystalline AgGaSe\(_2\) (MC) and an optical-quality single crystal of AgGaSe\(_2\) (OQ) found that the AgGaSe\(_2\) (MC) sample resulted in lower SHG responses, probably due to a higher defect concentration within the AgGaSe\(_2\) (MC) than the AgGaSe\(_2\) (OQ).\(^{176}\) Based on the findings in that work, Li\(_2\)CdGeS\(_4\) was compared to the AgGaSe\(_2\) (MC) due to the title material probably having a considerable defect concentration.\(^{176}\) Likewise, the SHG
responses of the Cu$_2$CdSnS$_4$ and α/β-Cu$_2$ZnSiS$_4$ were compared with that of AgGaSe$_2$ (MC). Although α/β-Cu$_2$ZnSiS$_4$ is a mixture, we confirmed that the NLO responses measured across various sample spots were reasonably consistent, indicating that the sample is homogeneous.

**4.2.9.2 Second Harmonic Generation**

Broadband SHG experiments were conducted at room temperature. In order to generate tunable pulses, coherent light of 1064 nm wavelength was first produced using an EKSPLA PL-2250 series diode-pumped Nd:YAG laser with a pulse width of 30 ps and a repetition rate of 50 Hz. The Nd:YAG laser pumped an EKSPLA Harmonics Unit (HU) H400 where the input beam was frequency tripled by a sum frequency generation scheme. The beam then entered an EKSPLA PG403-SH-DFG Optical Parametric Oscillator (OPO) composed of four main parts; a double-pass parametric generator, a single-pass parametric amplifier, a second harmonic generator (SH), and a difference frequency generation (DFG) scheme. The output wavelengths of the OPO used ranged from 1100 to 3300 nm at increments of 200 nm. The corresponding SHG wavelength range is therefore $\lambda_{\text{SHG}} = \lambda/2 = 550 - 1650$ nm.

The incident pulse energy was tuned to 15 μJ before being mildly focused onto samples with a spot size of roughly 0.5 mm in diameter by a CaF$_2$ convex lens. Here we determined the beam spot size in order to i) efficiently generate and properly average the SHG signals from powders of random orientations and to ii) minimize the change in the spot size when the fundamental wavelength, $\lambda$, is varied over a broad range (1100–3300 nm); the beam waist $w_0$ at the focus undergoes a significant $\lambda$-dependent variation via $w_0 = (\lambda/\pi)(f/\sigma)$, where $f$ and $\sigma$ are the focal length and the Gaussian width of the incident
beam, respectively. For wavelengths inaccessible with 15 μJ, the NLO counts were properly scaled in accordance with the measured SHG power dependence. The NLO signals from the samples were collected using a reflection geometry by a fiber optic bundle, which was coupled to a selective-grating (1800, 600, and 300 grooves/mm) spectrometer equipped with a charge-coupled device camera (Synapse) as well as an extended InGaAs (Symphony) detector. The overall detection range obtained from the combination of the two detectors was 300-2000 nm. Surface–induced effects as well as SHG signals from other optical components were negligible. Any thermal load on the samples by the laser pulses tuned below the bandgap was negligible due to its slow repetition rate of 50 Hz. The relative SHG signals spectrally resolved in a broad wavelength range were precisely calibrated with the known and measured efficiencies of all optical components.

Figure 4.5 shows the λ-dependent SHG responses from the title compounds. A dip near \( \lambda_{SHG} = 950–1050 \) nm is common to the samples and the reference, which arises from linear absorption of the fundamental beam by the container (capillary tubes), but this does not affect our estimation of the SHG coefficients. Significantly lower SHG counts for shorter wavelengths arise due to bandgap absorption of SHG light as well as multi-photon absorption (MPA) of the fundamental beam. Such a huge variance in the experimental SHG counts over the range of wavelengths, especially for Cu\(_2\)CdSnS\(_4\), clearly emphasizes the importance of the broadband approach for accurate NLO characterization. The size-dependent SHG counts for Cu\(_2\)CdSnS\(_4\) and \( \alpha/\beta \)-Cu\(_2\)ZnSiS\(_4\) are plotted in Figures 4.6 and 4.7, respectively, reconstructed from Figure 4.5. The results
show that both compounds are phase-matchable for longer wavelengths $\lambda_{\text{SHG}} \geq 1050$ nm and $\lambda_{\text{SHG}} \geq 850$ nm for Cu$_2$CdSn$_4$ and $\alpha/\beta$-Cu$_2$ZnSiS$_4$, respectively.

In order to estimate $\chi^{(2)}$ of Cu$_2$CdSn$_4$ and $\alpha/\beta$-Cu$_2$ZnSiS$_4$, the SHG counts must be compared at the static range in which both reference and sample are phase-matchable with minimal absorption effects. Using the Kurtz powder method$^{178}$ the static value of $\chi^{(2)}$ for the title compounds can be calculated by comparison with the reference according to:

$$\chi^{(2)}_S = \chi^{(2)}_R \times \left( \frac{I_{\text{SHG}}^S}{I_{\text{SHG}}^R} \right)^{1/2}, \quad (\text{Eq} \ 4.1)$$

where $I_{\text{SHG}}^S$ and $I_{\text{SHG}}^R$ are the measured SHG counts from the sample and the reference, respectively, at the same particle size, $d$. AgGaSe$_2$ is the benchmark mid-IR NLO material with a static SHG coefficient of $\chi^{(2)} = 66$ pm/V ($\lambda \rightarrow \infty$).$^{179,180}$ Our calculation yields a $\chi^{(2)}$ of 62±3 pm/V for Cu$_2$CdSn$_4$ and 15±2 pm/V for $\alpha/\beta$-Cu$_2$ZnSiS$_4$.

Figure 4.5. Broadband SHG spectra from Cu$_2$CdSn$_4$ (d=0-106 μm) [left] and $\alpha/\beta$-Cu$_2$ZnSiS$_4$ (d=0-150 μm) [right].
Cu₂CdSnS₄ exhibits phase-matching behavior for λ_{SHG} ≥ 1050 nm.

Cu₂ZnSiS₄ exhibits phase-matching behavior for λ_{SHG} ≥ 850 nm.

4.2.9.3 Third Harmonic Generation

Broadband THG experiments were conducted at room temperature with the same excitation source mentioned above for SHG measurements. The output wavelengths of
the OPO used in THG experiments ranged from 1300 nm to 3100 nm at increments of 200 nm. The corresponding wavelength ranges for THG is therefore $\lambda_{THG} = \lambda/3 = 433–1033$ nm. The incident pulse energy was tuned to 19 $\mu$J before being focused onto samples with a spot size of ~0.2 mm in diameter by a CaF$_2$ lens. Collection of THG light was performed in the same manner as mentioned above for SHG experiments. We confirmed that background THG from other optical components as well as frequency tripling by the NLO cascade were negligible. The relative THG signals spectrally resolved in a broad wavelength range were precisely calibrated with the known and measured efficiencies of all optical components (Figure 4.8). Being a higher-order NLO process, THG is much weaker than SHG; thus, the corresponding data collection time was 60 s. All data were scaled to the 1 s collection time.

In Figure 4.8 we plot relative THG counts of the samples as a function of $\lambda_{THG}$ in comparison with those from AgGaSe$_2$ on a semi-log scale at $d = 0$-$20$ $\mu$m. A dip near $\lambda_{THG} = 700$–$800$ nm arises from linear absorption of the fundamental beam by the container (capillary tubes). Note that a similar effect occurs for the SHG measurements. This effect does not affect our estimation of the THG coefficients. Because of the difference in bandgap energies and relevant linear absorption coefficients, we determined the THG coefficients of the samples at longer wavelengths, i.e., at the static limit ($\lambda \to \infty$), in which both linear absorption of THG and MPA are minimal.
Figure 4.8. Broadband THG ($d = 0$-$20 \, \mu m$) spectra from Cu$_2$CdSnS$_4$ (●), α/β-Cu$_2$ZnSiS$_4$ (◆), and AgGaSe$_2$ (○), respectively.

Figure 4.9. Particle size dependence of THG at $\lambda = 1800$ nm (left) and $\lambda = 2700$ nm (right) for Cu$_2$CdSnS$_4$ (●), α/β-Cu$_2$ZnSiS$_4$ (◆), and AgGaSe$_2$ (○), respectively.

The dots in Figure 4.9 correspond to the THG particle size dependence of AgGaSe$_2$ at $\lambda = 1800$ nm and 2700 nm. A decreasing trend with increasing $d$ clearly indicates non-phase-matched THG for $d > 20 \, \mu m$. Based on the Kurtz method, the
experimental THG coherence length is about $d_c = 32.5 \pm 12.5 \, \mu m$, which corresponds to the maximum THG counts. This value together with the reference value of $\chi_R^{(3)} = 1.6 \times 10^5 \, \text{pm}^2/\text{V}^2$ was used for estimating $\chi^{(3)}$ values of the samples. The squares in Figure 4.9 correspond to the case for Cu$_2$CdSnS$_4$. The $d$-dependence at 1800 nm is featureless because the phase-matching factor is washed out by strong bandgap absorption of THG light by the compound. However, at $\lambda = 2700 \, \text{nm}$, it indicates a non-phase-matching case, but with a relatively long THG coherence length of $d_c = 54 \pm 9 \, \mu m$. Note that the THG efficiency of Cu$_2$CdSnS$_4$ is significantly enhanced at 2700 nm compared to that at 1800 nm. The THG particle size dependence for $\alpha/\beta$-Cu$_2$ZnSiS$_4$ at these two input wavelengths also indicates a non-phase-matching case as plotted by the diamonds in Figure 4.9. Note that the THG coherence length increases from $d_c = 10 \pm 10 \, \mu m$ at 1800 nm to $d_c = 32.5 \pm 12.5 \, \mu m$ at 2700 nm. This trend is typical due to a reduced phase mismatch at longer wavelengths. We found that all samples and the reference are non-phase-matchable within our experimental range, although we only show the results for two incident wavelengths here.

The absolute $\chi^{(3)}$ value of the sample can be estimated by comparing with the reference using:

$$\chi_S^{(3)} = \chi_R^{(3)} \times \frac{(I_S^{\text{THG}}/I_R^{\text{THG}})^{1/2} \times (d_{c,R}/d_{c,S})}{},$$

(Eq 4.2)

where $I_S^{\text{THG}}$ and $I_R^{\text{THG}}$ are the measured THG counts from the sample and the reference at the same particle size and $d_{c,S}$ and $d_{c,R}$ are the corresponding coherence lengths determined from the data in Figure 4.9. Using $\chi_R^{(3)} = 1.6 \times 10^5 \, \text{pm}^2/\text{V}^2$, our calculation yields a $\chi^{(3)}$ for Cu$_2$CdSnS$_4$ of $\sim(0.8 \pm 0.2) \times 10^5 \, \text{pm}^2/\text{V}^2$ at 3100 nm, but this is very likely underestimated due to the bandgap absorption issue. The estimated $\chi^{(3)}$ for $\alpha/\beta$-
$\text{Cu}_2\text{ZnSiS}_4$ is $(0.21 \pm 0.06) \times 10^5 \text{ pm}^2/\text{V}^2$. This relatively low value is predicted due to its large bandgap.182

**4.2.9.4 Laser-Damage Threshold (LDT)**

In order to estimate damage thresholds of the compounds, SHG measurements were carried out on the samples with $d= 90 – 106 \text{ μm}$ as a function of laser intensity in the range of $0.3 – 17 \text{ GW/cm}^2$ using a typical Nd:YAG transition line of 1064 nm with a temporal pulse width of 30 ps. The damage threshold of a material significantly depends on the pulse width and here is a picosecond case. All experiments were conducted at room temperature.

The spectrally integrated SHG counts from $\text{Cu}_2\text{CdSnS}_4$ as a function of input intensity are shown in Figure 4.10. The dotted line represents the maximum SHG case in which fundamental depletion is absent, i.e. $I_{\text{SHG}} = aI^2$, where $I_{\text{SHG}}$ and $I$ are the SHG and fundamental intensities with $a$ being a proportionality constant that incorporates $|\chi^{(2)}|^2$. Although the compound has a high $\chi^{(2)}$ and $\chi^{(3)}$, it undergoes serious damage upon laser illumination due to efficient one-photon absorption (1PA) at 1064 nm (Figure 4.10). The LDT seems to be below 1 GW/cm$^2$. A similar experiment was conducted with an incident wavelength of 1300 nm, due to strong absorption at 1064 nm. The LDT of $\text{Cu}_2\text{CdSnS}_4$ was estimated as 0.2 GW/cm$^2$ at 1300 nm (Figure 4.15). We estimated the corresponding 2PA coefficient ($\sim$120 cm/GW) by fitting the measured SHG power dependence using a modified fundamental intensity by 2PA, $I_{2\text{PA}}$:

$$I_{\text{SHG}} = aI_{2\text{PA}}^2 \text{ with } I_{2\text{PA}} = I/[1 + I\beta d] \quad (\text{Eq 5.3})$$

Figure 5.15 also illustrates the case for $\alpha/\beta$-$\text{Cu}_2\text{ZnSiS}_4$. Considering the bandgap of the compound, we concluded that it undergoes three-photon absorption (3PA) of the
fundamental beam $I > 2 \text{ GW/cm}^2$, as evidenced by the deviation from the dotted line (maximum SHG). We estimated the corresponding 3PA coefficient $\gamma$ by fitting the measured SHG power dependence using a modified fundamental intensity by 3PA, $I_{3\text{PA}}$;

$$I_{\text{SHG}} = a I_{3\text{PA}}^2 \text{ with } I_{3\text{PA}} = \frac{I}{[1+2\gamma d I^2]^{1/2}}, \quad \text{(Eq 4.4)}$$

where $d = 90-106 \mu\text{m}$ is roughly the particle size for our reflection-based collection geometry and the constant, $a$, was carefully determined by fitting the low-intensity regime where 3PA is absent. The solid trace on top of the data points in Figure 5.15 is a fit using Equation S4, yielding $\gamma = 1.22 \text{ cm}^3/\text{GW}^2$. This value is higher than typical 3PA coefficients of inorganic materials having similar bandgaps.$^{183,184}$ This may arise from optical damage induced by significant 3PA.

Figure 4.10. SHG power dependence of Cu$_2$CdSnS$_4$ at 1064 nm.
Table 4.2. Comparison of SHG, THG, LDT, and phase matchability for Cu$_2$CdSnS$_4$, α/β-Cu$_2$ZnSiS$_4$, and AgGaSe$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\chi^{(2)}$ (pm/V)</th>
<th>Phase matching region (nm)</th>
<th>LDT (GW/cm$^2$)</th>
<th>THG $\chi^{(3)}$ (pm$^2$/V$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$CdSnS$_4$</td>
<td>62±3</td>
<td>$\lambda_{SHG} \geq 1050$</td>
<td>0.2</td>
<td>$(8.0\pm2.0) \times 10^4$</td>
</tr>
<tr>
<td>α/β-Cu$_2$ZnSiS$_4$</td>
<td>15±2</td>
<td>$\lambda_{SHG} \geq 850$</td>
<td>2.0</td>
<td>$(2.1\pm0.6) \times 10^4$</td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>66</td>
<td>$\lambda_{SHG} \geq 1550$</td>
<td>0.2</td>
<td>$1.6 \times 10^5$</td>
</tr>
</tbody>
</table>

### 4.2.10 Electronic Structure

The electronic structures of Cu$_2$CdSnS$_4$, α-Cu$_2$ZnSiS$_4$ and β-Cu$_2$ZnSiS$_4$ were calculated. Although calculations on Cu$_2$CdSnS$_4$ have previously been reported using VASP and the projector augmented wave (PAW) method with the Perdew, Burke, and Ernzerhof (PBE) exchange correlation approximation and the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional, our calculations expand upon those previously reported, particularly the partial density of states (PDOS) contributions. The electronic structures of α-Cu$_2$ZnSiS$_4$ and β-Cu$_2$ZnSiS$_4$ have been previously calculated. Here CASTEP was used to determine the electronic band structures of α-Cu$_2$ZnSiS$_4$ and β-Cu$_2$ZnSiS$_4$; the bandgap energies were found to be closer to the experimental bandgap energies than those previously calculated. Additionally, an exchange potential, the modified Becke-Johnson (mBJ) potential for improving bandgap determination in semiconductors, was employed within the WIEN2k software. All of the calculated bandgap values are markedly underestimated which is a well-known problem of DFT calculations using the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA).
4.2.10.1 CASTEP

The refined crystal structures of $\text{Cu}_2\text{CdSnS}_4$, $\alpha$-$\text{Cu}_2\text{ZnSiS}_4$, and $\beta$-$\text{Cu}_2\text{ZnSiS}_4$ were used for the electronic structure calculations carried out using the total-energy code of CASTEP to determine the electronic band structure as well as density of states (DOS) (Figure 4.11). In addition, quantitative bond analysis was performed.\textsuperscript{188,189} In CASTEP, the total energy is calculated using the plane-wave pseudopotential method within density functional theory (DFT). The PBE-GGA was used to treat the exchange and correlation effects.\textsuperscript{190} Using this method, the interactions between the ionic cores and the electrons are described by norm-conserving pseudopotentials.\textsuperscript{191} The number of plane-waves included in the basis set was determined by a cutoff energy of 600 eV for all compounds. The numerical integration of the Brillouin zone was performed using a $5\times5\times6$, $3\times4\times4$ and $4\times4\times3$ Monkhorst-Pack k-point sampling for $\text{Cu}_2\text{CdSnS}_4$, $\alpha$-$\text{Cu}_2\text{ZnSiS}_4$ and $\beta$-$\text{Cu}_2\text{ZnSiS}_4$, respectively. The self-consistent field (SCF) tolerance was set to $1 \times 10^{-6}$ eV/atom for the convergence criteria and 100 cycles were performed. The interpolation integration method was used for the DOS analysis. For all compounds, a Mulliken bond population analysis within the CASTEP code was used to calculate the bond orders (Table 4.3).\textsuperscript{192,193} Direct bandgaps of 0.69 eV and 1.69 eV at the $\Gamma$-point were calculated for $\text{Cu}_2\text{CdSnS}_4$ and $\alpha$-$\text{Cu}_2\text{ZnSiS}_4$. An indirect band gap of 2.23 eV was calculated for $\beta$-$\text{Cu}_2\text{ZnSiS}_4$. 


Figure 4.11. Calculated electronic band structure shown on the left of each plot and TDOS and PDOS (electrons/eV) shown on the right side of each plot using CASTEP. The dotted line denotes the Fermi level (E_F).

Table 4.3. The Mulliken bond population data.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Cu₂CdSnS₄</td>
<td>0.37</td>
<td>NA</td>
<td>0.32</td>
<td>NA</td>
<td>0.49</td>
</tr>
<tr>
<td>α-Cu₂ZnSiS₄</td>
<td>0.36</td>
<td>0.42</td>
<td>NA</td>
<td>0.70</td>
<td>NA</td>
</tr>
<tr>
<td>β-Cu₂ZnSiS₄</td>
<td>0.37</td>
<td>0.42</td>
<td>NA</td>
<td>0.69</td>
<td>NA</td>
</tr>
</tbody>
</table>

The total DOS (TDOS) and PDOS for Cu₂CdSnS₄ are shown in Figure 4.11. The valence band region from -10 to -7.5 eV chiefly originates from Cd-4d orbitals along with minor contributions from the S-3s, S-3p, Sn-5s, and Sn-5p orbitals, whereas the states in the region from -7.5 to -6.0 eV mainly arise from S-3s, S-3p, Sn-5s, and Sn-5p orbitals. Approaching the top of the valence band from -6.0 to -2.5 eV, the states are largely due to S-3p, Sn-5p, Cu-4d orbitals with lesser influence from Sn-5s, Cd-5s, Cu-4s, and Cu-3p orbitals. The states in the highest energy valence band region closest to the Fermi level (E_F), -2.5 to 0 eV, primarily arise from the S-3p, Sn-5p, and Cu-4d orbitals, with slight contributions from S-3s, Sn-5s, Cd-4p, Cu-5s and Cu-3p orbitals. The minimum states in the conduction band 0.69 to 2.5 eV are mainly attributed to S-3p and Sn-5s orbitals. Higher in the conduction band from 2.5 to 5 eV, the states are principally
from the Sn-5s orbitals along with donations from the S-3p, Sn-5s, and Cu-3p orbitals and very small contributions from the S-3s, Cd-5s, Cd-4p, and Cu-4s. From 5.0 to 10 eV the states evolve largely from the Sn-5p, Sn-5s, S-3p, and Cu-3p orbitals, with additional contributions from S-3s, Cd-5s, and Cd-4p orbitals. The Cd orbitals in Cu₂CdSnS₄ and the Zn orbitals in α-Cu₂ZnSiS₄ have an extremely small contribution to the Eᵢₐₜ.

4.2.10.2 WIEN2k

The band structure and DOS of Cu₂CdSnS₄, α-Cu₂ZnSiS₄ and β-Cu₂ZnSiS₄ were also carried out using the WIEN2k package, which utilizes the full-potential linearized augmented plane-wave method (FLAPW) within DFT for solving the Kohn-Sham equations for total energy (Figure 4.12). The PBE-GGA was used to treat the exchange and correlation effects; in addition the mBJ exchange potential was used to achieve greater accuracy of the bandgap energies in semiconductors. In these calculations, the muffin tin radii (RMT) of Cu, Zn, Si, and S were set to 2.39, 2.40, 1.85, and 1.96 bohr, respectively. With respect to Cu₂CdSnS₄, the RMT values were set to 2.39, 2.50, 2.49, and 1.96 bohr, respectively for Cu, Cd, Sn, and S. SCF calculations converged when the energy difference between successive iterations fell below 0.1 mRy/unit cell. Additionally, a total of 3,000 k-points were used in the full Brillouin zone for each compound, which corresponded to 336, 630, and 240 k-points in the irreducible Brillouin zone (iBZ) for the Cu₂CdSnS₄, α-Cu₂ZnSiS₄ and β-Cu₂ZnSiS₄ structures, respectively.
Figure 4.12. Calculated electronic band structure shown on the left of each plot and TDOS and PDOS (states/eV) shown on the right side of each plot using WIEN2k.

The dotted line denotes the Fermi level (E\(_F\)).

The bandgap for \(\alpha\)-Cu\(_2\)ZnSiS\(_4\) was previously calculated to be 1.3 eV using WIEN2k. Here, the electronic structures of \(\alpha\)-Cu\(_2\)ZnSiS\(_4\) and \(\beta\)-Cu\(_2\)ZnSiS\(_4\) were recalculated using the WIEN2k software but with the addition of the mBJ potential, which resulted in better agreement between calculated and experimental bandgap values.\(^{186}\) Using this potential, direct bandgaps of 0.79 eV, 2.05, and 2.57 eV at the \(\Gamma\)-point were calculated for Cu\(_2\)CdSnS\(_4\), \(\alpha\)-Cu\(_2\)ZnSiS\(_4\), and \(\beta\)-Cu\(_2\)ZnSiS\(_4\), respectively. Inclusion of the mBJ potential, however, barely alters the TDOS and PDOS for \(\alpha\)-Cu\(_2\)ZnSiS\(_4\) and \(\beta\)-Cu\(_2\)ZnSiS\(_4\). Additionally, when the PDOS was calculated using the mBJ potential in the WIEN2k software, the PDOS contributions are very similar to the description already described in Rosmus et al.\(^{161}\) The discrepancy in the nature of the band gap for \(\beta\)-Cu\(_2\)ZnSiS\(_4\) (direct versus indirect) results from using two software packages that employ different methods. However, it should be noted that the band structures obtained using both methods indicate a number of low energy transitions for the compound that are closely spaced in energy.
Table 4.4. Comparison of calculated bandgap energies using WIEN2k (PBE-GGA), WIEN2k (PBE-GGA+mBJ), and CASTEP (PBE-GGA).

<table>
<thead>
<tr>
<th>Compound</th>
<th>WIEN2k PBE-GGA Bandgap energy (eV)</th>
<th>WIEN2k PBE-GGA+mBJ Bandgap energy (eV)</th>
<th>CASTEP PBE-GGA Bandgap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₂CdSnS₄</td>
<td>0.79 direct</td>
<td>0.69 direct</td>
<td></td>
</tr>
<tr>
<td>α-Cu₂ZnSiS₄</td>
<td>1.3 direct¹⁶¹</td>
<td>2.05 direct</td>
<td>1.69 direct</td>
</tr>
<tr>
<td>β-Cu₂ZnSiS₄</td>
<td>1.7 direct¹⁶¹</td>
<td>2.57 direct</td>
<td>2.23 indirect</td>
</tr>
</tbody>
</table>

4.3 Results and Discussion

The structure of Cu₂CdSnS₄ was determined using single crystal X-ray diffraction. The compound crystallizes with the stannite structure, a derivative of cubic diamond. This is in close agreement with the structure of the mineral cernyite, Cu₂Cd₀.₃⁷Zn₀.₃₃Fe₀.₂₉Mn₀.₀₀₅SnS₄,¹⁹⁷ and the reported lattice parameters.¹⁹⁸ The wurtz-stannite structure of α-Cu₂ZnSiS₄ and the wurtz-kesterite structure of β-Cu₂ZnSiS₄ are derived from hexagonal diamond.¹⁶⁰ While every S²⁻ is surrounded by one Zn²⁺ or Cd²⁺, one Si⁴⁺ or Sn⁴⁺ and two Cu⁺ ions in each compound, the cation ordering patterns differ (Figure 4.13).

Figure 4.13. The three-dimensional diamond-like structures.
Synchrotron powder diffraction indicates that Cu$_2$CdSnS$_4$ is nearly phase pure and the ~60:40 α- and β-Cu$_2$ZnSiS$_4$ sample contains ~0.3% ZnS (Figure 4.1). Thus far, α- and β-Cu$_2$ZnSiS$_4$ have not been isolated due to similar ground state energies that impose synthetic limitations.\textsuperscript{160b} Cu$_2$CdSnS$_4$ melts congruently at 930 °C and α/β-Cu$_2$ZnSiS$_4$ exhibits higher thermal stability with a melting point over 1000 °C (Figure 5.3). Cu$_2$CdSnS$_4$ was found to have an optical bandgap of 0.92 eV (Figure 5.4). The bandgaps have been estimated as ~3.0 and ~3.2 eV for α- and β-Cu$_2$ZnSiS$_4$, respectively.\textsuperscript{160b}

Figure 4.14. UV-Vis-NIR (left) and FT-IR (right) spectra.

The title compounds exhibit wide optical transparency, exceeding AgGaSe$_2$ (0.76-17 μm), AgGaS$_2$ (0.48-11.4 μm) and ZnGeP$_2$ (0.74-12 μm).\textsuperscript{152b} Cu$_2$CdSnS$_4$ and α/β-Cu$_2$ZnSiS$_4$ are transparent from 1.2-25 μm and 0.7-25 μm, respectively (Figure 2). While some new SHG materials have narrower transparency windows, such as Na$_2$Ge$_2$Se$_5$ (0.521-18.2 μm)\textsuperscript{154f} and K$_2$P$_2$Se$_6$ (0.596-19.8 μm),\textsuperscript{154g} others have comparable ranges.\textsuperscript{154b,d}

The phase matchability of Cu$_2$CdSnS$_4$ and α/β-Cu$_2$ZnSiS$_4$ were evaluated by measuring SHG with broadband incident λ of 1100-3300 nm (λ$_{\text{SHG}}$ = 550-1650 nm) for
particle sizes ≤ 106 and ≤ 150 μm, respectively (Figure 4.5). The SHG response for 
Cu$_2$CdSnS$_4$ rises with increasing particle size (i.e. is PM) at $\lambda_{\text{SHG}} \geq 1050$ nm (Figure 4.6).$^{199}$ $\alpha/\beta$-Cu$_2$ZnSiS$_4$ has a larger range of phase matchability, $\lambda_{\text{SHG}} \geq 850$ nm (Figure 4.7). These PM regions, which are wider than AgGaSe$_2$ ($\lambda_{\text{SHG}} \geq 1550$ nm), can benefit wave-mixing applications.$^{200}$ Using AgGaSe$_2$ as a reference, the $\chi^{(2)}$ values of Cu$_2$CdSnS$_4$ and $\alpha/\beta$-Cu$_2$ZnSiS$_4$ were found to be 62±3 and 15±2 pm/V, respectively (Figure 5.15). The $\chi^{(2)}$ of Cu$_2$CdSnS$_4$ is comparable to that of AgGaSe$_2$ (66 pm/V) and notably larger than that of AgGaS$_2$.

Third-order nonlinearity is attractive for applications in all-optical switching and optical image processing in the visible and IR.$^{201}$ The potential of the title compounds for these types of applications was examined by measuring third harmonic generation (THG), and the $\chi^{(3)}$ values were estimated by the powder method.$^{155\text{g,h}}$ While SHG materials are commonly used in frequency mixing setups to access wider frequency ranges, THG materials can greatly improve processing speeds.

![Figure 4.15. Broadband SHG and SHG power dependence of Cu$_2$CdSnS$_4$ (●), $\alpha/\beta$-Cu$_2$ZnSiS$_4$ (♦), and AgGaSe$_2$ (●). $\lambda = 1064$ nm for ● and ●. $\lambda = 1300$ nm for ●.](image)

The THG responses (Figure 4.8) for the samples and AgGaSe$_2$ all intensify with increasing $\lambda$. The THG efficiencies likely improve in the deeper mid-IR, especially for
Cu$_2$CdSnS$_4$ since all of the THG responses were measured above the bandgap. Due to bandgap absorption, the $\chi^{(3)}$ for Cu$_2$CdSnS$_4$ [(8.0±2.0) × 10$^4$ pm$^2$/V$^2$] is likely underestimated. Owing to the wide bandgap of $\alpha/\beta$-Cu$_2$ZnSiS$_4$, the THG efficiencies [$\chi^{(3)} = (2.1\pm0.6) \times 10^4$ pm$^2$/V$^2$] are unrestricted in the measured region. It was confirmed that THG is NPM for both compounds as well as the reference within the experimental range $\lambda = 1300 – 3100$ nm (Figure 4.9), which is typical due to a large phase-mismatch between $\lambda$ and $\lambda_{THG}$. Although these $\chi^{(3)}$ values are lower than that of AgGaSe$_2$ (1.6 × 10$^5$ pm$^2$/V$^2$), practical use in applications relies on high LDT.

To assess LDTs, spectrally integrated SHG counts for Cu$_2$CdSnS$_4$ and $\alpha/\beta$-Cu$_2$ZnSiS$_4$ were plotted versus input intensity under picosecond laser excitation (Figure 4.15). The dashed lines represent the maximum SHG case where fundamental depletion is absent. Although Cu$_2$CdSnS$_4$ has high $\chi^{(2)}$ and $\chi^{(3)}$, it suffers serious damage upon picosecond laser exposure due to one-photon absorption at 1064 nm (Figure 4.10). The LDT of Cu$_2$CdSnS$_4$ (0.2 GW/cm$^2$ at 1300 nm) is akin to AgGaSe$_2$ (0.2 GW/cm$^2$ at 1064 nm). The LDT of $\alpha/\beta$-Cu$_2$ZnSiS$_4$ (2.0 GW/cm$^2$) is one order of magnitude larger than AgGaSe$_2$. This progress is credited to the wide bandgap as laser damage results from three-photon absorption (3PA).

An electronic structure calculation was reported for Cu$_2$CdSnS$_4$, but here we expand upon the partial density of states (PDOS), in addition to using the modified Becke-Johnson exchange potential for all compounds (Table 4.4). The direct bandgaps of Cu$_2$CdSnS$_4$ and $\alpha$-Cu$_2$ZnSiS$_4$ were calculated as 0.79 and 2.05 eV, respectively. The calculated direct bandgap of $\beta$-Cu$_2$ZnSiS$_4$ is 2.57 eV. The differences in the electronic structures of Cu$_2$CdSnS$_4$ and $\alpha/\beta$-Cu$_2$ZnSiS$_4$ can be understood by examining the PDOS.
(Figures 4.16, 4.11 and 4.12). The largest discrepancy near the Fermi level ($E_F$) arises from the contributions of the IV ion orbitals at the conduction band minimum (CBM). For $\alpha$-Cu$_2$ZnSiS$_4$ the states at the CBM chiefly arise from S-$p$, Si-$s$, Si-$p$ and Zn-$s$ orbitals, with lesser contributions from the Zn-$p$ and Cu-$p$ orbitals; the PDOS for $\beta$-Cu$_2$ZnSiS$_4$ is similar to that of $\alpha$-Cu$_2$ZnSiS$_4$ (Figures 4.11 and 4.12). However, in Cu$_2$CdSnS$_4$ the lowest energy states in the CBM evolve predominantly from the Sn-$s$ and S-$p$ orbitals.

![Density of States Diagram](image)

**Figure 4.16.** The TDOS and PDOS (electrons/eV). The dotted line denotes the Fermi level ($E_F$).

### 4.4 Conclusions

In summary, Cu$_2$CdSnS$_4$ and $\alpha/\beta$-Cu$_2$ZnSiS$_4$ exhibit critical criteria for useful NLO materials. The $\chi^{(2)}$, $\chi^{(3)}$ and LDT of Cu$_2$CdSnS$_4$ are similar to those of AgGaSe$_2$. While the $\chi^{(2)}$ and $\chi^{(3)}$ of $\alpha/\beta$-Cu$_2$ZnSiS$_4$ are lower, it outshines benchmark IR NLO materials in LDT. These results align with the ideas that a higher degree of covalency leads to larger NLO susceptibility,\textsuperscript{204} while a wider bandgap leads to better LDT. Yet,
high NLO susceptibility and LDT are not mutually exclusive. Indeed, we recently revealed strong SHG, THG, and LDT for Li$_2$CdGeS$_4$.\textsuperscript{205} To access useful NLO materials, a firmer grasp on the interplay between bonding, bandgap, nonlinear susceptibility, and LDT must be established. Based on our results, we propose targeting compounds with a higher degree of covalency without much decrease in bandgap. For the title compounds, the largest disparity of Mulliken bond populations arises in the IV-S bonds, where the Sn-S bond order is 0.49 and Si-S is ~0.7 (Table 4.3). In this system, improvements could be accomplished by tuning the composition to increase the level of covalency without much change in the states near the E$_F$.

4.5 References


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5. Characterization of metal-sulfur bonding in $\alpha$/$\beta$-$\text{Cu}_2\text{ZnSiS}_4$ and $\text{Cu}_2\text{CdSiS}_4$ by X-ray photoelectron spectroscopy on single crystals and density functional theory calculations.

5.1 Introduction

Compared to binary and ternary diamond-like semiconductors (DLSs), quaternary DLSs have an increased compositional flexibility, due to the greater number of cations and anions in the structure, which allows for properties to be tuned to target technological applications. Quaternary DLSs with the formula I$_2$-II-IV-VI$_4$ have attractive physicochemical properties that suggest potential in the fields of photovoltaics,\textsuperscript{206-209} thermoelectrics,\textsuperscript{210-212} and nonlinear optics.\textsuperscript{213-216}

In the area of photovoltaics, the quaternary DLSs Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSe) have been proposed as next-generation solar cell materials, substituting CuIn$_{1-x}$Ga$_x$S$_2$ (CIGS) as the absorber layer in thin-film solar cells. One appealing feature of CTZS and CZTSe is the bandgaps, which lie between 1.0 and 1.5 eV.\textsuperscript{217-221} In addition, the high abundance and low toxicity of Zn and Sn make CZTS and CZTSe viable alternatives.\textsuperscript{217-221} Furthermore, efficiencies which have been recently achieved are impressive for research in its early stages. The efficiency was found to be 8.4% for CZTS, where thin films were grown on Mo-coated soda lime glass substrates by a vacuum thermal evaporation method.\textsuperscript{222} On the other hand, CZTSe, synthesized via electrodeposition of stacked metal precursors followed by selenization, was found to have an efficiency of 5%.\textsuperscript{223} However, a solid solution of Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$ produced by a hydrazine solution-based process, exhibited an efficiency of 11.1%,\textsuperscript{224} which is approaching the record efficiency of 19.9% reported for CIGS,\textsuperscript{225} thus further investigations are necessary to enhance the efficiency.
Copper-based quaternary DLSs with formula of Cu$_2$-II-IV-VI$_4$, where II= Co, Zn, Cd; IV= Ge, Sn; VI= S, Se, Te, are showing promising thermoelectric (TE) properties due to the distorted chalcopyrite-like structures, which allow for relatively low lattice thermal conductivities.\textsuperscript{226-233} The quaternary CZTS and Cu$_2$CoZnS$_4$ prepared as nanocrystals resulted in ZT values of 0.05 and 0.46 at 700 K, respectively.\textsuperscript{229} However, nickel-doped Cu$_2$ZnSnS$_4$ showed an increase in ZT, 0.37 at 700 K.\textsuperscript{229} Additionally, the ZT increased to 0.36 at 700 K when CZTS was prepared with a copper rich stoichiometry, Cu$_{2.1}$Zn$_{0.9}$SnS$_4$.\textsuperscript{230} CZTSe, Cu$_2$ZnGeSe$_4$, and Cu$_2$CdSnSe$_4$ were found to have ZT values of 0.18, 0.19, and 0.55 at ~700 K.\textsuperscript{227,228} Again, the ZT value increased with either substitution or additional copper incorporation into the formula. For example, Cu$_{2.1}$Zn$_{0.9}$In$_{0.1}$Se$_4$ and Cu$_{2.1}$Zn$_{0.9}$SnSe$_4$ have ZT values of 0.37 and 0.36 at 700 K, both exceeding 0.18 at 700 K for the undoped CZTSe.\textsuperscript{227,232} Quaternary copper DLSs are providing a new generation of potential candidates for TE devices, but higher ZT values will be needed. Recently, density functional theory (DFT) have been employed to calculate the ZT values of Cu$_2$ZnSnVI$_4$, where VI= S, Se, and Te, these types of DFT studies may eventually allow for other quaternary DLSs to be selectively targeted for potential use in TE devices.\textsuperscript{234,235}

Recently, two copper-based quaternary DLSs, α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSnS$_4$, have found to be of practical use for infrared nonlinear optical (NLO) applications due to their elevated thermal stabilities, wide optical transparency ranges, broad regions of phase matchability for second harmonic generation, and large laser damage thresholds (Rosmus et al.\textsuperscript{216} and Chapter 4). However, to be used in practical laser devices, large crack-free single crystals will need to be grown.
The rising popularity of copper-based quaternary DLSs as candidate materials for several important applications increases the need to develop structure-property relationships among these materials. An increase in our fundamental understanding of these materials will help researchers to better target DLS materials for specific applications. Here we have selected \( \alpha/\beta-Cu_2ZnSiS_4 \) and \( Cu_2CdSiS_4 \) as a case study, to investigate the use of X-ray photoelectron spectroscopy (XPS) on single crystals of the title compounds and electronic structure calculations for understanding metal-sulfur (M-S) bonding in these materials.

The quaternary DLS, \( \alpha/\beta-Cu_2ZnSiS_4 \) has garnered increased attention in the past several years. In addition to its nonlinear optical properties described above, several reports have recently appeared in the literature. The single crystal X-ray structure solution and refinement of \( \alpha-Cu_2ZnSiS_4 \) was reported in 2011 showing that the compound crystallizes with the wurtz-stannite crystal structure in the noncentrosymmetric space group \( Pmn2_1 \) (see Chapter 2).\(^{236}\) In 2012, another polymorph, \( \beta-Cu_2ZnSiS_4 \), with the wurtz-kesterite (\( Pn \)) crystal structure was discovered via Rietveld refinement of synchrotron powder diffraction data.\(^{237}\) Single crystals of \( Cu_2ZnSiS_4 \) were studied via polarization-dependent piezoreflectance (PzR),\(^{238}\) surface photovoltage (SPV) spectroscopy,\(^{239,240}\) and electrolyte electroreflectance (EER) by Levcenco et al.\(^{241}\) The cadmium analog, \( Cu_2CdSiS_4 \), was first synthesized in 1967 and the crystal structure was published in 1972.\(^{242,243}\) \( Cu_2CdSiS_4 \) with the lattice parameters of \( a = 7.598(8) \) Å, \( b = 6.486(6) \) Å, and \( c = 6.26(1) \) Å is isostructural with \( \alpha-Cu_2ZnSiS_4 \).\(^{244}\) This structure-type was confirmed in 1974 by Schafer and Nitche.\(^{244}\) The melting point of \( Cu_2CdSiS_4 \) was
found to be 978 °C in 1999 by Piskach et al.; however, after this time, new measurements have not been reported for Cu₂CdSiS₄.

Here, we demonstrate how relatively small, but well formed single crystals of the title compounds can be prepared. XPS was performed on those single crystals to verify the oxidation states of the elements and gain insight on the (M-S) bonding. The nature of the M-S bonding was further investigated through the use of electronic structure (ES) calculations. The ESs of α/β-Cu₂ZnSiS₄ have been described in Rosmus et al., Chapter 3, and Chapter 5. However, the ES calculations of Cu₂CdSiS₄ are described here for the first time. Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) and high-resolution synchrotron X-ray powder diffraction data are also reported.

5.2 Experimental

5.2.1 Reagents

Copper powder, 99.999%, Strem, Newburyport, MA; cadmium powder, 99.999%, Strem Newburyport, MA; silicon powder, 99.999%, Strem, Newburyport, MA; sulfur powder, sublimed, 99.5%, Fisher Scientific, Pittsburgh, PA; zinc powder, 99.999%, Strem, Newburyport, MA

5.2.2 Synthesis

High-temperature, solid-state synthesis was carried out to prepare α/β-Cu₂ZnSiS₄ and Cu₂CdSiS₄. The starting materials were weighed in stoichiometric amounts and ground in an agate mortar and pestle for 30 minutes in an argon-filled glove box. Each sample was placed into a graphite crucible, which was then inserted into a 12 mm outer
diameter fused-silica tube. The tube was flamed-sealed under a vacuum of $10^{-3}$ mbar using an oxy-methane torch. The heating profile for $\alpha/\beta$-Cu$_2$ZnSiS$_4$, found in Rosmus et al.,$^{237}$ was also used to prepare Cu$_2$CdSiS$_4$. Both reactions produced crystals that were further analyzed with SEM/EDS and XPS.

5.2.3. Optical Images

Optical images of $\alpha/\beta$-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSnS$_4$ single crystals were collected using a Keyence Digital Microscope System, VHX-600. Images with increased depth of field were obtained by using the Keyence Profile Measurement Unit VHX-S15 with an antivibration system. The Keyence VH-Z100R Real Zoom Lens with magnification range of x100 – x1000 was used.

5.2.4. High-Resolution Synchrotron X-ray Powder Diffraction

High-resolution synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using an average wavelength of 0.413838 Å for a powdered sample of Cu$_2$CdSiS$_4$. Discrete detectors covering an angular range from -6 to 16° 2θ were scanned over a 34° 2θ range, with data points collected every 0.001° 2θ and a scan speed of 0.01°/s. The 11-BM instrument uses X-ray optics with two platinum-stripped mirrors and a double-crystal Si(111) monochromator, where the second crystal has an adjustable sagittal bend.$^{246}$ Ion chambers monitor incident flux. A vertical Huber 480 goniometer, equipped with a Heidenhain encoder, positions an analyzer system comprised of twelve perfect Si(111) analyzers and twelve Oxford-Danfysik LaCl$_3$ scintillators, with a spacing of 2° 2θ.$^{247}$ The sample was spun during data collection. A Mitsubishi robotic arm was used to mount and dismount the sample on the diffractometer.$^{248}$ Data were collected at room temperature.
The diffractometer was controlled via EPICS\textsuperscript{249} and data were collected while continually scanning the diffractometer 2θ arm. A mixture of NIST standard reference materials, Si (SRM 640c) and Al\textsubscript{2}O\textsubscript{3} (SRM 676) was used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Corrections were applied for detector sensitivity, 2θ offset, small differences in wavelength between detectors, and the source intensity, as noted by the ion chamber before merging the data into a single set of intensities evenly spaced in 2θ. Rietveld refinements were carried out with GSAS/EXPGUI.\textsuperscript{166,250}

The starting model for Cu\textsubscript{2}CdSiS\textsubscript{4} was obtained from Chapuis et al.\textsuperscript{243} The background was fitted with a shifted Chebyschev polynomial with 18 terms.\textsuperscript{251} The peak shapes were accounted for through refinement of the Lorentzian terms within the type-3 profile. Lattice parameters, atomic coordinates, and isotropic displacement parameters were refined.

5.2.5. Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS)

Scanning electron micrographs were obtained using a Tescan Vega scanning electron microscope, with a working distance of ~15 mm and an accelerating voltage of 20 kV. Semi-quantitative elemental analysis for Cu\textsubscript{2}CdSiS\textsubscript{4} was executed using a Hitachi S-3400 N scanning electron microscope equipped with a Bruker Quantax model 400 energy dispersive spectrometer using an XFlash® 5010 EDS detector with a 129 eV resolution. Single crystals of Cu\textsubscript{2}CdSiS\textsubscript{4} were attached to double-sided carbon tape that was adhered onto an aluminum specimen holder. Three crystals of each sample were selected for semi-quantitative EDS analysis. Spectra were collected for three areas on each Cu\textsubscript{2}CdSiS\textsubscript{4} crystal at an accelerating voltage of 15 kV for 5 min live time at a
working distance of 10 mm. When determining the composition, the oxygen and the carbon from the carbon tape and the aluminum from the specimen holder were subtracted to acquire a composition based on only the elements within the crystals. EDS elemental analysis of $\alpha/\beta$-Cu$_2$ZnSiS$_4$ was reported by Rosmus et al.$^{216}$

**5.2.6. X-ray Photoelectron Spectroscopy (XPS)**

XPS was performed using a Thermo Scientific K-Alpha XPS instrument possessing monochromatized Al K$_\alpha$ radiation with a wavelength of 8.3386 Å (1486.7 eV), operating at 12 kV and 6 mA with an energy resolution of $<0.85$ eV. The instrument uses a hemispherical electron energy analyzer equipped with a 128-channel detector system. Data were collected and processed using the Avantage software package from Thermo Scientific. Copper, silver, and gold calibration standards that are built into the sample stage were sputtered with 1000 eV argon ions to remove residual surface contamination and used to calibrate the energy scale via an automated instrument calibration routine that uses the Ag 3$d_{5/2}$, Au 4$f_{7/2}$, and Cu 2$p_{3/2}$ peaks. Crystals were mounted onto a thin sheet of aluminum using vacuum-compatible, double-sided, carbon tape. Samples were sputtered with 1000 eV argon ions until the O 1$s$ peak from surface oxidation was no longer detected or barely present. It is estimated that the samples were sputtered approximately 7000 Å relative to SiO$_2$. Ten scans were collected for survey spectra from -5.00 to 1350 eV binding energy (BE). For $\alpha/\beta$-Cu$_2$ZnSiS$_4$ high-resolution scans were preformed for the Cu 2$p$ and LM2 Auger, Zn 2$p$, Si 2$p$ and 2$s$, S 2$p$, C 1$s$, O 1$s$, and Ar 2$p$ peaks. It should be noted that no attempt was made to differentiate between $\alpha$- and $\beta$-Cu$_2$ZnSiS$_4$ crystals. Multiple crystals were measured and the BEs were found to be the same. In the case of Cu$_2$CdSiS$_4$ the same high-resolutions scans were obtained
except that in place of Zn 2p the Cd 3d was collected. Survey spectra and high-resolution spectra were obtained with an analyzer pass energy of 200 eV and 50 eV, respectively. The base pressure in the analysis chamber was typically $2 \times 10^{-9}$ mbar or lower. An X-ray spot size of 40 μm was used. All spectra were acquired with the charge neutralization flood gun turned on. The flood gun uses a combination of low energy electrons and argon ions. Spectra were charge corrected using adventitious carbon 1s peak at 285.0 eV. Reported BEs were measured with a precision of ± 0.2 eV or better. Peak fitting was performed using mixed Gaussian/Lorentzian peak shapes and a Shirley-type background.

5.2.7. Electronic Structure

5.2.7.1 CASTEP

The crystal structure of Cu$_2$CdSiS$_4$ was used for the ES calculation. The ES calculations of Cu$_2$CdSiS$_4$ were carried out using the total-energy code of CASTEP, which allows for the determination of band structure, density of states and, quantitative bond analysis. In CASTEP, the total energy is calculated using the plane-wave pseudopotential method of density functional theory (DFT). The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) was used to treat the exchange and correlation effects. Using this method, the interactions between the ionic cores and the electrons are described by norm-conserving pseudopotentials. The following orbital electrons were treated as valence electrons: Cu $4s^23p^63d^9$, Cd $5s^24p^64d^{10}$, Si $3s^23p^2$, and S $3s^23p^4$. Using a cutoff energy of 600 eV, the number of plane-waves included in the basis set was determined. The numerical integration of the Brillouin zone was performed using a $3 \times 4 \times 4$ Monkhorst-Pack k-point sampling. The self-consistent field (SCF) tolerance was set to $1 \times 10^{-6}$ eV/atom for the convergence
criteria and 100 cycles were performed. The interpolation integration method was used for the density of states (DOS) analysis. A Mulliken bond population analysis within the CASTEP code was used to calculate the bond orders.\textsuperscript{255,256}

\textbf{5.2.7.2 WIEN2K}

The electronic band structure and DOS were also calculated for Cu\textsubscript{2}CdSiS\textsubscript{4} using the WIEN2k package, which utilizes the full-potential linearized augmented plane-wave method (FLAPW) within density functional theory (DFT) for solving the Kohn-Sham equations for total energy.\textsuperscript{257-259} PBE-GGA was used to treat the exchange and correlation effects; in addition the modified Becke-Johnson (mBJ) exchange potential was used to achieve greater accuracy of the bandgap.\textsuperscript{260} In these calculations, the muffin tin radii (RMT) of Cu, Cd, Si, and S were set to 2.23, 2.50, 1.93, and 1.97 bohr respectively. SCF calculations converged when the energy difference between successive iterations fell below 0.1 mRy/unit cell. The geometry of the structure was optimized. Additionally, a total of 1,000 k-points was used in the full Brillouin zone (BZ), which corresponded to 240 k-points within the irreducible Brillouin zone (iBZ). Despite the use of the mBJ, the calculated bandgap energy is still markedly underestimated which is a well-known problem of DFT calculations using the PBE-GGA.\textsuperscript{261} The electronic structures of α-Cu\textsubscript{2}ZnSiS\textsubscript{4} and β-Cu\textsubscript{2}ZnSiS\textsubscript{4} can be found in Rosmus et al.\textsuperscript{216}

\textbf{5.3 Results and Discussion}

\textbf{5.3.1 Synthesis and Phase Identification}

The high-temperature, solid-state syntheses of α/β-Cu\textsubscript{2}ZnSiS\textsubscript{4} and Cu\textsubscript{2}CdSiS\textsubscript{4} produced well formed single crystals by slow cooling. Optical images of the single
crystals are shown in Figure 5.1. The crystals of \(0.25 \times 0.25 \times 0.10\) mm in size had surfaces that were large enough to perform XPS measurements on them.

Figure 5.1. Optical images of \(\alpha/\beta-Cu_2ZnSiS_4\) and \(Cu_2CdSiS_4\).

Synchrotron X-ray powder diffraction of the \(Cu_2ZnSiS_4\) product proved to be critical in the determination of the two polymorphs for this system\(^{237}\), therefore, high-resolution synchrotron X-ray powder diffraction data were also collected on the ground crystals of \(Cu_2CdSiS_4\). From the Rietveld refinement of the synchrotron X-ray powder diffraction data it was determined that only one phase was present in the sample. \(Cu_2CdSiS_4\) is isostructural to \(\alpha-Cu_2ZnSiS_4\), crystallizing in the wurtz-stannite structure with the orthorhombic, noncentrosymmetric space group \(Pmn2_1\). There were several weak peaks that were unable to be identified. These peaks were so weak that they were only observable in the synchrotron diffraction data; they could not be found in the laboratory X-ray powder diffraction data. The final refinement converged with \(\chi^2 = 3.713\), \(R_p = 0.1070\) (all data) and \(R_{wp} = 0.1257\) (all data), Figure 5.2.
Figure 5.2. The Rietveld refinement results for Cu$_2$CdSiS$_4$ using high-resolution synchrotron powder diffraction data. In the plot, the observed data (+) and the calculated data (red solid line) are shown at the top. Below the data is one row of tick marks (!) corresponding to the locations of the expected Bragg reflections for Cu$_2$CdSiS$_4$. The difference between the observed and the calculated patterns (green solid line) is shown at the bottom.

Figure 5.3 shows a scanning electron micrograph obtained for a Cu$_2$CdSiS$_4$ crystal (Figure 5.3, inset). Additionally, EDS was performed on crystals of Cu$_2$CdSiS$_4$; no other elements were detected in the crystals (Figure 5.3) and the composition was found to be Cu$_{2.1}$Cd$_{1.0}$Si$_{0.9}$S$_{3.5}$, which is close to the nominal composition. EDS data were collected on crystals of $\alpha/\beta$-Cu$_2$ZnSiS$_4$ as previously reported in Rosmus et al. The composition was found to be Cu$_{2.1}$Zn$_{1.0}$Si$_{0.9}$S$_{3.5}$ for $\alpha/\beta$-Cu$_2$ZnSiS$_4$. These results are identical to
those found for Cu$_2$CdSiS$_4$. Additionally, elemental mapping was carried out on multiple crystals, where each was found to demonstrate a homogenous mixture of the elements.

![Energy dispersive spectrum](image)

**Figure 5.3.** Representative energy dispersive spectrum for Cu$_2$CdSiS$_4$, with the inset showing a scanning electron micrograph for a small Cu$_2$CdSiS$_4$ crystal.

### 5.3.2 XPS Analysis

XPS spectra for α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ were analyzed to elucidate the oxidation states of the elements. As we have observed with several other chalcogenide samples, the surface oxidation/contamination in sulfide and selenide materials can be quite significant. Initial low-resolution scans of the title crystals were performed and while the core level features for each element could be observed, a very strong O 1$s$ peak at about 532 eV was prominent in the spectrum. Therefore Ag$^+$ ion sputtering was employed to remove the surface oxidation layer, so that the bulk material could be assessed. Low-resolution scans were performed every so often until it was determined that sputtering ~7000 Å relative to SiO$_2$ could remove the surface contamination, yet no shift was observed in the core level peaks for Cu, Zn/Cd, Si and S.
Figure 5.4. (a) Cu 2\(p_{1/2}\) and Cu 2\(p_{3/2}\), (b) Zn 2\(p_{1/2}\) and Zn 2\(p_{3/2}\), (c) Si 2\(p\), and (d) S 2\(p_{1/2}\), S 2\(p_{3/2}\), and Si 2\(s\) XPS spectra for \(\alpha/\beta\)-Cu\(_2\)ZnSiS\(_4\).

Figure 5.5. (a) Cu 2\(p_{1/2}\) and Cu 2\(p_{3/2}\), (b) Cd 3\(d_{3/2}\) and Cd 3\(d_{5/2}\), (c) Si 2\(p\), and (d) S 2\(p_{1/2}\), S2\(p_{3/2}\), and Si 2\(s\) XPS spectra for Cu\(_2\)CdSiS\(_4\).
Table 5.1. Core-line BEs (eV) of Cu 2p$_{1/2}$ and Cu 2p$_{3/2}$ for the title compounds and selected copper-containing materials.

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<th>Cu 2p$_{3/2}$ BE (eV)</th>
<th>Ref.</th>
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</tbody>
</table>

The Cu 2p spectra for α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ displayed BEs that correspond to the spin-orbit-split, Cu 2p$_{1/2}$ and Cu 2p$_{3/2}$ peaks. The Cu 2p$_{1/2}$ BE were found to be 952.8 and 952.9 eV, while the BEs of Cu 2p$_{3/2}$ were 933.0 and 933.1 eV for α/β-Cu$_2$ZnSiS$_4$ (Figure 5.3a) and Cu$_2$CdSiS$_4$ (Figure 5.4a), respectively. Selected copper-containing materials were used to compare the BEs to the title compounds, Table 5.1. The BEs of the binary DLS, Cu$_2$S, are similar to those found for α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$. The values found for the Cu 2p$_{3/2}$ peak for the title compounds are also close to that found for the ternary DLS, CuInS$_2$. The Cu 2p$_{1/2}$ and Cu 2p$_{3/2}$ BEs of Cu$_2$ZnSnS$_4$, a similar quaternary DLS, were reported by Wang et al to be 951.4 eV and 931.6 eV, respectively. These values for Cu$_2$ZnSnS$_4$ are ~0.5 eV less than those found by Zhang and coworkers; however, they are still reasonably comparable. XPS data for Cu$_2$CdSnS$_4$ prepared as nanoparticles and nanorods can be found in Table 5.2. By simple comparison with other copper +1 containing materials the copper ions in α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ can be tentatively assigned the +1 charge. However, assigning copper a +1 charge is not straightforward and comparison with the BEs of other related
materials could lead to incorrect assignment. A shake-up satellite peak between 940-945 eV (Figure 5.6) for copper is a tell-tale sign of Cu$^{2+}$. The lack of this shake-up peak in our data is indicative of Cu$^{+}$ and therefore we can definitively assign that oxidation based on these data.$^{263}$

![Figure 5.6](image)

**Figure 5.6.** XPS spectra of copper metal (Cu$^{0}$), Cu$_2$O (Cu$^{1+}$), CuO (Cu$^{2+}$), and CuAl$_2$O$_4$ (Cu$^{2+}$) from bottom to top showing the Cu 2p$_{3/2}$ and shake-up satellite peaks.$^{263}$

**Table 5.2.** Core-line BEs (eV) of Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$ for selected zinc-containing materials.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Zn 2p$_{1/2}$ BE (eV)</th>
<th>Zn 2p$_{3/2}$ BE (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha/\beta$-Cu$_2$ZnSiS$_4$</td>
<td>1045.65</td>
<td>1022.61</td>
<td>this work</td>
</tr>
<tr>
<td>Zn metal</td>
<td>1044.0</td>
<td>1021.0</td>
<td>269</td>
</tr>
<tr>
<td>ZnS</td>
<td>-</td>
<td>1022.0</td>
<td>270</td>
</tr>
<tr>
<td>ZnSe</td>
<td>-</td>
<td>1021.8</td>
<td>265</td>
</tr>
<tr>
<td>ZnO</td>
<td>1045.9</td>
<td>1022.8</td>
<td>271</td>
</tr>
<tr>
<td>Cu$_2$ZnSnS$_4$</td>
<td>1046.0</td>
<td>1023.0</td>
<td>272</td>
</tr>
<tr>
<td>Cu$_2$ZnSnS$_4$</td>
<td>1045.6</td>
<td>1021.5</td>
<td>269</td>
</tr>
<tr>
<td>Cu$_2$(Zn,Fe)SnS$_4$</td>
<td>1045.1</td>
<td>1022.0</td>
<td>273</td>
</tr>
</tbody>
</table>

For $\alpha/\beta$-Cu$_2$ZnSiS$_4$, the Zn 2p spectra consisted of the Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$ peaks, which were found to have BEs of 1045.65 and 1022.61 eV (Figure 5.3b), respectively.
The Zn 2p$_{3/2}$ peaks for the binary compounds in Table 5.2 have BEs~0.7 eV lower than $\alpha/\beta$-Cu$_2$ZnSiS$_4$ and when comparing to ZnO, 0.2 eV greater.$^{265,270,271}$ The BEs of the quaternary compounds for the Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$ peaks are close to that found for $\alpha/\beta$-Cu$_2$ZnSiS$_4$, where the BEs for Cu$_2$ZnSnS$_4$ reported by Langer et al. are nearly identical.$^{269}$ It has been noted that the BE values for Zn can change for very thin films on certain substrates and for very small particles due to interface effects and particle size effect, respectively; however, the thin film samples and nanoparticle samples that we have compared our values to seem to match well and should probably not be considered as very thin or very small. It has been also noted the Zn 2p$_{3/2}$ suffers from overlap with Zn metal, but in this case the full width at half maximum (FWHM) is a tell-tale signature, where the width for Zn$^{2+}$ should be larger than in the native metal.$^{274}$ However, the FWHM is of course affected somewhat by the pass energy to make matters more complex; however the difference seems to be relatively large. Biesinger et al. reports that when a pass energy of 10 eV and 20 eV is used the FWHM for the 2p$_{3/2}$ of Zn metal is 0.82 and 0.86, respectively while that of Zn$^{2+}$ is 1.55 and 1.60.$^{274}$ Here, using a pass energy of 50 eV, the FWHM for $\alpha/\beta$-Cu$_2$ZnSiS$_4$ was found to be 1.67 eV and 1.81 eV for Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$, respectively, which is clearly indicative of Zn$^{2+}$. 
Table 5.3. Core-line BEs (eV) of Cd 3d\(_{3/2}\) and Cd 3d\(_{5/2}\) for selected cadmium-containing materials.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cd 3d(_{3/2}) BE (eV)</th>
<th>Cd 3d(_{5/2}) BE (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_2)CdSiS(_4)</td>
<td>412.7</td>
<td>405.9</td>
<td>this work</td>
</tr>
<tr>
<td>CdS</td>
<td>412.0</td>
<td>405.2</td>
<td>275</td>
</tr>
<tr>
<td>CdS</td>
<td>-</td>
<td>405.3</td>
<td>272</td>
</tr>
<tr>
<td>CdSe</td>
<td>-</td>
<td>405.3</td>
<td>272</td>
</tr>
<tr>
<td>CdTe</td>
<td>412.0</td>
<td>405.2</td>
<td>276</td>
</tr>
<tr>
<td>CdIn(_2)S(_2)Se(_4)</td>
<td>412.5</td>
<td>405.8</td>
<td>277</td>
</tr>
<tr>
<td>Cu(_2)CdSnS(_4)</td>
<td>411.7</td>
<td>404.9</td>
<td>267</td>
</tr>
<tr>
<td>Cu(_2)CdSnS(_4)</td>
<td>411.4</td>
<td>404.8</td>
<td>268</td>
</tr>
</tbody>
</table>

For Cu\(_2\)CdSiS\(_4\), the Cd 3d spectrum contains the Cd 3d\(_{3/2}\) and Cd 3d\(_{5/2}\) peaks that were found to have BEs of 412.7 and 405.9 eV (Figure 5.4b), respectively. The oxidation state of the Cd in Cu\(_2\)CdSiS\(_4\) was found to be +2 based on similar BE values found for other divalent-cadmium-containing materials in the literature. For example, the BE for the Cd 3d\(_{5/2}\) peak in CdIn\(_2\)S\(_2\)Se\(_4\) was reported as 405.8 eV by Malitesta et al.\(^\text{277}\) The binary cadmium-containing DLSs have a slightly lower BE.\(^\text{272,275,276}\) Additional comparisons to the Cd 3d\(_{3/2}\) and Cd 3d\(_{5/2}\) peaks for Cu\(_2\)CdSiS\(_4\) can be found in Table 5.3.

Table 5.4. Core-line BEs (eV) of Si 2p for selected silicon-containing materials.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si 2p BE (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α/β-Cu(_2)ZnSiS(_4)</td>
<td>102.1</td>
<td>this work</td>
</tr>
<tr>
<td>Cu(_2)CdSiS(_4)</td>
<td>101.9</td>
<td>this work</td>
</tr>
<tr>
<td>SiO(_x)</td>
<td>101.9</td>
<td>278</td>
</tr>
<tr>
<td>Si(_3)N(_4)</td>
<td>102.0</td>
<td>279</td>
</tr>
<tr>
<td>(PbF(<em>2))(</em>{15.6})(PbO)(_{36.0})(SiO(<em>2))(</em>{28.4})</td>
<td>101.8</td>
<td>280</td>
</tr>
<tr>
<td>(MoO(<em>3))(</em>{90})(SiO(<em>2))(</em>{10})</td>
<td>102.2</td>
<td>281</td>
</tr>
<tr>
<td>Li(_2)Si(_3)</td>
<td>101.3</td>
<td>282</td>
</tr>
</tbody>
</table>

The Si 2p spectra exhibited BEs of 102.1 and 101.9 eV for α/β-Cu\(_2\)ZnSiS\(_4\) (Figure 5.3c) and Cu\(_2\)CdSiS\(_4\) (Figure 5.4c), respectively. The Si 2s core-line peak BE is 153.11
and 153.42 eV for \(\alpha/\beta\)-Cu\(_2\)ZnSiS\(_4\) (Figure 5.3d) and Cu\(_2\)CdSiS\(_4\) (Figure 5.4d), respectively. A Si 2s peak with a BE of 154.08 eV was found for SiO\(_2\), which is close to the values found here for the two compounds.\(^{283}\) A comparison of the BEs for the Si 2p peak can be found in Table 5.4. SiO\(_x\) and Si\(_3\)N\(_4\) were found to have Si 2p BEs very similar to Cu\(_2\)CdSiS\(_4\) and \(\alpha/\beta\)-Cu\(_2\)ZnSiS\(_4\).\(^{278,279}\) For (MoO\(_3\))\(_{90}\)(SiO)\(_{10}\), the Si 2p BE reported at 102.2 eV is akin to the BE found for \(\alpha/\beta\)-Cu\(_2\)ZnSiS\(_4\).\(^{279\text{ }}\) The BE for an oxidation state of 4+ for Si has been reported at slightly lower values (101.8 eV and 101.3 eV) for (PbF\(_2\))\(_{15.6}\)(PbO)\(_{56.0}\)(SiO\(_2\))\(_{28.4}\) and Li\(_2\)SiS\(_3\), respectively.\(^{280,282}\)

**Table 5.5. Core-line BEs (eV) of S 2p for selected sulfur-containing materials.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>S 2p BE (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_2)ZnSiS(_4)</td>
<td>162.8</td>
<td>this work</td>
</tr>
<tr>
<td>Cu(_2)CdSiS(_4)</td>
<td>162.7</td>
<td>this work</td>
</tr>
<tr>
<td>Cu(_2)S</td>
<td>162.6</td>
<td>263</td>
</tr>
<tr>
<td>ZnS</td>
<td>162.4</td>
<td>284</td>
</tr>
<tr>
<td>CoS</td>
<td>162.6</td>
<td>284</td>
</tr>
<tr>
<td>MoS(_2)</td>
<td>162.4</td>
<td>285</td>
</tr>
</tbody>
</table>

The S 2p spectra showed a broad peak fitted to two components, S 2p\(_{1/2}\) and S 2p\(_{3/2}\), the S 2p BE was found to be 162.8 and 162.7 eV for \(\alpha/\beta\)-Cu\(_2\)ZnSiS\(_4\) (Figure 5.3d) and Cu\(_2\)CdSiS\(_4\) (Figure 5.4d), respectively. The BEs found for the title compounds are compared to other materials in Table 5.5. The S 2p BEs were reported to be 162.6 eV for Cu\(_2\)S and CoS.\(^{263}\) The binary MoS\(_2\) and ZnS, as well as the ternary CuInS\(_2\) have slightly lower reported BEs of 162.4 eV.\(^{264,284,285}\)
5.3.4 Electronic Structure

Electronic structure calculations for Cu$_2$CdSiS$_4$ have been performed for the first time. From the electronic band structure calculated using CASTEP, Cu$_2$CdSiS$_4$ was determined to be a direct band gap semiconductor at the Γ-point with an energy of 1.75 eV, Figure 5.7 (left). The band structure diagram calculated using WIEN2k also indicated a direct band gap transition at the Γ-point (Eg = 1.93 eV), Figure 5.8 (left). The total and partial DOS was also calculated for Cu$_2$CdSiS$_4$ and examined to determine the orbital contributions. The partial DOS calculated using CASTEP were found to be comparable to those obtained from the WIEK2k calculations; only small differences exist. The PDOS obtained using CASTEP shows a larger contribution of the Cu-$p$, Cd-$p$, and Si-$p$ states at the bottom of the conduction band. Additionally there are some minor differences between the two PDOS plots for the Cd-$d$ states in the region from -3 to -7 eV. The results from CASTEP are shown in Figure 5.7 (right) and those using WIEN2k are shown in Figure 5.8 (right).
Figure 5.7. Calculated electronic band structure of Cu$_2$CdSiS$_4$ using CASTEP (left). Total and partial DOS (electrons/eV) for Cu$_2$CdSiS$_4$ (right). The dotted line denotes the Fermi level ($E_F$).

Figure 5.8. Calculated electronic band structure of Cu$_2$CdSiS$_4$ using WIEN2k (left). Total and partial DOS (states/eV) for Cu$_2$CdSiS$_4$ (right). The dotted line denotes the Fermi level ($E_F$).

The valence band region from -10 to -9 eV primarily arises from Cd-$d$ orbitals along with lesser contributions from S-$s$ and S-$p$ orbitals and minor influence from Si-$s$
and Si-\(p\) orbitals. From -9 to -7 eV, states chiefly originate from the Si-\(s\), S-\(s\), and S-\(p\) orbitals. Si-\(p\), Cd-\(d\), and S-\(p\) orbitals have a large contribution in the region from -7 to -2 eV, with lesser influence from Si-\(s\), Cd-\(s\), Cd-\(p\), Cu-\(s\), and Cu-\(p\) orbitals. As previously found with the Cu-III-VI\(_2\) chalcopyrite DLSs, the wurtz-kesterite-type Ag\(_2\)ZnSiS\(_4\) and \(\beta\)-Cu\(_2\)ZnSiS\(_4\), along with the wurtz-stannite-type \(\alpha\)-Cu\(_2\)ZnSiS\(_4\), the top of the valence band of Cu\(_2\)CdSiS\(_4\) is dominated by the hybridization of the coinage metal-\(d\) and chalcogen-\(p\) states with minor inputs from the other orbitals.\(^{237,286,287}\) At the bottom of the conduction band, the largest donations arise from the Si-\(s\), Si-\(p\), S-\(p\), Cd-\(s\) orbitals, with influence from the Cd-\(p\), and Cu-\(p\) orbitals, and small input from the Cu-\(s\) and S-\(s\) orbitals. Higher in the conduction band, the Cd-\(p\) and Cu-\(p\) orbitals become more prominent, while S-\(p\) orbitals remain constant and the influence of the Si-\(s\) and Si-\(p\) orbitals decrease. The total and partial DOS for Cu\(_2\)CdSiS\(_4\) are comparable to that of the isostructural \(\alpha\)-Cu\(_2\)ZnSiS\(_4\),\(^{216,237}\) Of course there are differences in the contributions of the orbitals that belong to Cd and Zn-\(d\); however, these differences mainly occur deep in the valence band. Additionally, there are slight differences in the contributions of the Si-\(s\) and S-\(p\) states in the energy region of -9 to -7 eV.

The partial DOS for \(\alpha\)-Cu\(_2\)ZnSiS\(_4\) and \(\beta\)-Cu\(_2\)ZnSiS\(_4\) are nearly equivalent, except for at the bottom of the conduction band, where for \(\beta\)-Cu\(_2\)ZnSiS\(_4\) there are larger contributions of the Zn-\(s\) and Si-\(s\) states.\(^{216}\) The lack of variation is not surprising due to \(\alpha\)-Cu\(_2\)ZnSiS\(_4\) and \(\beta\)-Cu\(_2\)ZnSiS\(_4\) differing only in cation ordering. As a result, their bonding environments should be similar, which was verified by the Mulliken bond population analysis for \(\alpha\)-Cu\(_2\)ZnSiS\(_4\) and \(\beta\)-Cu\(_2\)ZnSiS\(_4\), which were found to be nearly
identical. Hence, it was reasonable not to have tried to differentiate between the \(\alpha\)-Cu\(_2\)ZnSiS\(_4\) and \(\beta\)-Cu\(_2\)ZnSiS\(_4\) crystals when performing XPS measurements.

**Table 5.6. The Mulliken bond population data.**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_2)CdSiS(_4)</td>
<td>0.36</td>
<td>NA</td>
<td>0.44</td>
<td>0.69</td>
</tr>
<tr>
<td>(\alpha)-Cu(_2)ZnSiS(_4)(^{216})</td>
<td>0.36</td>
<td>0.42</td>
<td>NA</td>
<td>0.70</td>
</tr>
<tr>
<td>(\beta)-Cu(_2)ZnSiS(_4)(^{216})</td>
<td>0.37</td>
<td>0.42</td>
<td>NA</td>
<td>0.69</td>
</tr>
</tbody>
</table>

The bond orders for Cu\(_2\)CdSiS\(_4\) were calculated to be 0.36 for Cu-S, 0.44 for Cd-S, and 0.69 for Si-S. The bond orders are equivalent to those found for \(\alpha\)-Cu\(_2\)ZnSiS\(_4\) and \(\beta\)-Cu\(_2\)ZnSiS\(_4\), which suggests that the level of iono-covalency is similar in these materials (Table 5.6). In addition, the iono-covalency was investigated through comparison of the BEs found for the title compounds and the BEs of copper-, zinc-, cadmium-, silicon-, and sulfur-containing materials found in the NIST database (Figures 7-8).\(^{288}\)

**Figure 5.9.** A plot of BE comparisons for Cu \(2p_{3/2}\).\(^{288}\) The yellow line indicates the BE values for \(\alpha/\beta\)-Cu\(_2\)ZnSiS\(_4\) and Cu\(_2\)CdSiS\(_4\).

In Figure 5.9, BEs are plotted versus a range of ionic (Cu-F) to covalent (Cu-Cu) bonding interactions. As stated earlier, the \(2p_{3/2}\) BEs for Cu cannot be used to definitely
determine oxidation state because there is some overlap between Cu$^0$, Cu$^{1+}$, and Cu$^{2+}$ values. The bonding interactions of the title compounds were found to have a relatively greater degree of covalency than some other copper-containing materials as shown in Figure 5.9. Additionally, smaller BEs for Cu-S generally occur when the copper has an oxidation of +2, whereas larger BEs for the Cu-S correlate to an oxidation of +1. The BEs found for α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ are at the top of the range of the Cu-S containing compounds where the copper has an oxidation state of +1.

![Figure 5.10](image)

**Figure 5.10.** A plot of BE comparisons for Si 2$p$ (left) and S 2$p$ (right). The yellow lines indicate the BE values for α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$.

The comparison of BEs of silicon-containing compounds that all contain Si$^{4+}$ to the title compounds is shown in Figure 5.10, left. This demonstrates that the silicon-sulfur bonding interactions in α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ are like those found for silicon-oxygen in SiO$_x$ materials, and not strictly covalent like Si$^0$, or highly covalent like those for SiC. Similarly, the S 2$p$ BEs of α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ were compared to those of other sulfur-containing materials, where the sulfur is in -2 oxidation state, see Figure 5.10 right. It can be seen that the S 2$p$ BEs of the title compounds are similar to the BEs found for sulfur in ZnS. It is worth noting that the S 2$p$ BEs of the title
compounds are akin to the lower values reported for ZnS and transition metal sulfides. This indicates that the M-S interactions in the title DLSs are not very covalent such as those found for elemental sulfur, B$_2$S$_3$, or As$_2$S$_3$ yet they are not on the very ionic end of the spectrum.

The bonding interactions found for $\alpha/\beta$-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ through using XPS data indicated that the title materials have a greater degree of covalency than some other copper-containing materials. The silicon interactions were found to be like that of SiO$_x$ materials, and not covalent like Si$^0$ and the M-S the interactions were found to be iono-covalent. The bonding interactions found via XPS data corresponded with the Mulliken bond population analysis, which resulted in bond orders for $\alpha/\beta$-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ to in the iono-covalent range.

5.4 Conclusions

Samples of $\alpha/\beta$-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ have been prepared via high-temperature, solid-state synthesis. Refinement of synchrotron powder diffraction data revealed that the sample of Cu$_2$CdSiS$_4$ showed only one phase crystallizing in the wurtz-stannite structure, in the noncentrosymmetric space group P$_{mn21}$. Single crystals with a size $\sim$100-400 $\mu$m of $\alpha/\beta$-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ were characterized using XPS. The oxidation states were verified to correspond to +1 for copper, +2 for zinc/cadmium, +4 for silicon, and -2 for sulfur. The BEs of the title compounds were also compared to other copper-, zinc-, cadmium-, silicon-, and sulfur-containing materials to investigate the iono-covalency. Based on this comparison the M-S bonding in these DLS has a relatively greater degree of covalency than some other metal sulfides. Additionally, the bond orders of the two compounds obtained from DFT calculations were comparable,
where $\alpha/\beta$-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ exhibited ioni-covalency. The ES calculations were performed for the first time for Cu$_2$CdSiS$_4$. The band structure calculated via CASTEP was found to have a direct gap at the $\Gamma$-point with energy of 1.75 eV. A comparison of the DOS of $\alpha/\beta$-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ revealed insignificant differences between the contributions of the elements around the Fermi level. Recently, the wide band gap $\alpha/\beta$-Cu$_2$ZnSiS$_4$ was shown to have large laser damage threshold (LDT), 2.0 GW/cm$^2$. Due to the similarity between the title compounds, there is reason to believe that Cu$_2$CdSiS$_4$ may also have a large LDT; however, due to electronic band structure calculations showing a lower band gap energy for Cu$_2$CdSiS$_4$, the second-order nonlinear optical susceptibility ($\chi^{(2)}$) may result in a higher value than what was found for $\alpha/\beta$-Cu$_2$ZnSiS$_4$ ($\chi^{(2)} = 15 \pm 2$ pm/V).

5.5 References


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6. Structure and optical properties of Mn-substituted AgInSe$_2$ chalcopyrite semiconductors

6.1 Introduction

AgInSe$_2$ is of considerable interest for technological applications, such as near infrared nonlinear optics, optical detectors, Schottky diodes, solar cells, etc. The potential for these applications are based on the outstanding optical and electrical properties, e.g., direct band gap (~1.2 eV), high optical absorption (~$10^{-5}$ cm$^{-1}$), capability of pn-control, and relatively high mobility. Although, all of these characteristics are better than those of CuInSe$_2$-based materials that are commercially available for solar cell applications, there have been few reports concerning AgInSe$_2$. The investigations of chemical substitutions in CuInSe$_2$, for example CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS), have resulted in improved properties. Therefore, substitutions in the AgInSe$_2$ system can be exploited to render the above characteristics, which are advantageous for PV devices, even more attractive.

Substitutions in the AgInSe$_2$ system can, not only provide avenues for improving properties, but reduce cost. Currently the applications of AgInSe$_2$ are limited due to the expensive constituent elements, Ag and In. Recent work has demonstrated that a substantial amount of cations in the I-III-VI$_2$ chalcopyrites can be replaced by inexpensive transition metal ions, such as Mn and Fe in CuInSe$_2$ and CuInS$_2$. Here, we validate the idea of transition metal substitution in AgInSe$_2$ using manganese as an example. The introduction of transition metal ions, such as Mn, may impart favorable magnetic interactions in the parent semiconductor, opening up the possibility of using AgInSe$_2$ as a potential host material for spintronic and magneto-optic applications. Due to the distinct properties of manganese compared to silver and indium, the crystal
structure, X-ray photoelectron spectra, magnetic properties, optical diffuse reflectance spectra, and electronic structure have been systematically studied in this work for the Mn-substituted AgInSe$_2$ materials.

6.2 Experimental

6.2.1 Reagents

Silver powder, -325 mesh, 99.99%, Cerac, Mayfield Heights, OH; indium powder, -325 mesh, 99.99%, Strem, Newburyport, MA; manganese powder, 0.8-3mm, 99.99%, Cerac, Mayfield Heights, OH; and selenium powder, -325 mesh, 99.99%, Strem, Newburyport, MA.

6.2.2 Synthesis

High-temperature, solid-state synthesis was used to prepare AgInSe$_2$, Ag$_{1-x}$Mn$_x$InSe$_2$ ($x=0.05, 0.10, and 0.15$) and Ag$_{1-2x}$Mn$_x$InSe$_2$ ($x=0.015, 0.03, 0.05, 0.07, and 0.10$). The starting materials were weighed and ground in an agate mortar and pestle for 30 min in an argon-filled glove box and then poured into a 9 mm outer diameter fused-silica tube. The tube was then transferred to a 12 mm outer diameter fused-silica tube. The tube was flame-sealed under vacuum ($\sim 10^{-4}$ mbar) using an oxy-methane torch. Samples of the Ag$_{1-2x}$Mn$_x$InSe$_2$ series were heated to 850 °C in 8 h, held at 850 °C for 72 h, and then cooled to ambient temperature in 8 h. Samples of the Ag$_{1-x}$Mn$_x$InSe$_2$ series were heated using the same profile, but were later annealed at 520 °C for 200 h.

6.2.3 Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDS)

Semi-quantitative elemental analysis for AgInSe$_2$, Ag$_{1-x}$Mn$_x$InSe$_2$ ($x=0.05$), and Ag$_{1-2x}$Mn$_x$InSe$_2$ ($x=0.015-0.07$) was carried out using a Hitachi S-3400 N scanning
electron microscope equipped with a Bruker Quantax model 400 energy dispersive spectrometer using an XFlash® 5010 EDS detector with a 129 eV resolution. All samples were placed on double-sided carbon tape that was adhered to an aluminum specimen holder. Three pieces of each sample ingot were selected for semi-quantitative EDS analysis. Spectra were collected for three areas on each piece at an accelerating voltage of 15 kV for 5 min live time at a working distance of 10 mm.

6.2.4 X-ray Powder Diffraction (XRPD)

AgInSe₂, Ag₁₋ₓMnₓInSe₂, and Ag₁₋₂ₓMnₓInSe₂ were first ground in an agate mortar and pestle, and then ground with silicon powder, an internal standard reference, obtained from the Gem Dugout. XRPD patterns were collected using a PANalytical X’pert PRO MPD X-ray powder diffractometer with the X’celerator detector operating at 45 kV and 40 mA in the Bragg-Brentano geometry using Cu Kα radiation. A 0.25° divergence slit, 0.5° anti-scatter slit, and a 0.02 rad Soller slit were used for both incident and diffracted beams. Diffraction data were collected from 15 to 145° 2θ with a step width of 0.008° and a time per step of 100 s. Phase identification was performed using X’pert High ScorePlus³⁰⁷ and the International Centre for Diffraction Data (ICDD) powder diffraction file database.

Using XRPD data, the Rietveld refinements for phase-pure samples of AgInSe₂, Ag₁₋₂ₓMnₓInSe₂ (x=0.015-0.07), and Ag₁₋ₓMnₓInSe₂ (x=0.05) were carried out using GSAS/EXPGUI.³⁰⁸,³⁰⁹ Crystal structures of AgInSe₂³¹⁰ and Si were used as starting models. For each model, lattice parameters, selenium x-coordinate (x₆e), site occupation factors (SOFs), atomic displacement parameters (Uᵢₗₒ), peak shape, and background were refined. The shifted Chebyshev polynomial with 12-15 terms was used to fit the
A pseudo-Voigt function with the Finger-Cox-Jephcoat asymmetry correction was used to model the peak profiles. The $U_{\text{iso}}$ values were refined independently for each ion in AgInSe$_2$, Ag$_{1-x}$Mn$_x$InSe$_2$, and Ag$_{1-2x}$Mn$_x$InSe$_2$, except for the Ag and Mn, which were constrained to be equal due to the Mn being on the Ag site. Initially, the SOFs for all ions were freely refined for AgInSe$_2$; however, in the final refinements, SOF$_{\text{In}(4b)}$ was constrained to one, since freely refining SOF$_{\text{In}(4b)}$ resulted in unrealistic SOFs, slightly greater than one. In the case of Ag$_{1-2x}$Mn$_x$InSe$_2$, to rule out alternative hypotheses other than that of Mn residing on the Ag site, several other models were tested. When Mn was placed on the In site, with the sum of the SOF$_{\text{Mn}(4b)}$ and SOF$_{\text{In}(4b)}$ constrained to 1, the refinements resulted in a negative or nearly zero SOF$_{\text{Mn}(4b)}$, suggesting that the Mn does not occupy the In site. However, when Mn was placed on the Ag site, all SOFs were constrained to the values of the nominal composition, the refinement converged well. The least-squares refinements converged for all data with the lattice parameters, $x_{\text{Se}}$, SOFs, $U_{\text{iso}}$, $\chi^2$, $R_p$ and $wR_p$ reported in Table 6.1.
Table 6.1. Structural parameters and refinement details for AgInSe$_2$ and Ag$_{1-2x}$Mn$_x$InSe$_2$ obtained from Rietveld refinement using X-ray powder diffraction data.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>AgInSe$_2$</th>
<th>Ag$_{1-2x}$Mn$_x$InSe$_2$ x=0.015</th>
<th>Ag$_{1-2x}$Mn$_x$InSe$_2$ x=0.03</th>
<th>Ag$_{1-2x}$Mn$_x$InSe$_2$ x=0.05</th>
<th>Ag$_{1-2x}$Mn$_x$InSe$_2$ x=0.07</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice Parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-axis(Å)</td>
<td>6.1040(2)</td>
<td>6.0981(1)</td>
<td>6.0929(3)</td>
<td>6.0837(1)</td>
<td>6.0746(1)</td>
</tr>
<tr>
<td>c-axis(Å)</td>
<td>11.7116(5)</td>
<td>11.7080(5)</td>
<td>11.7084(3)</td>
<td>11.7017(3)</td>
<td>11.6972(4)</td>
</tr>
<tr>
<td>Volume(Å$^3$)</td>
<td>436.35(2)</td>
<td>435.38(2)</td>
<td>434.66(1)</td>
<td>433.10(1)</td>
<td>431.63(1)</td>
</tr>
<tr>
<td>c/a</td>
<td>1.919(1)</td>
<td>1.91994(9)</td>
<td>1.922(1)</td>
<td>1.92345(6)</td>
<td>1.92559(7)</td>
</tr>
<tr>
<td><strong>Cation 4a</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOF(Ag/Mn)</td>
<td>0.95(1)/0</td>
<td>0.97/0.015</td>
<td>0.94/0.03</td>
<td>0.90/0.05</td>
<td>0.86/0.07</td>
</tr>
<tr>
<td>100$U_{ios}$(Å$^2$)</td>
<td>2.07(7)</td>
<td>4.7(2)</td>
<td>1.34(9)</td>
<td>2.6(4)</td>
<td>1.3(1)</td>
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<tr>
<td><strong>Cation 4b</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOF(In)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>100$U_{ios}$(Å$^2$)</td>
<td>4.7(1)</td>
<td>1.79(8)</td>
<td>4.9(2)</td>
<td>2.6(3)</td>
<td>5.1(2)</td>
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<td><strong>Anion 8d</strong></td>
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<tr>
<td>SOF(Se)</td>
<td>0.984(6)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>100$U_{ios}$(Å$^2$)</td>
<td>3.65(9)</td>
<td>3.6(1)</td>
<td>3.1(1)</td>
<td>2.6(1)</td>
<td>2.4(1)</td>
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<tr>
<td>$x_{Se}$</td>
<td>0.246(5)</td>
<td>0.250(3)</td>
<td>0.256(2)</td>
<td>0.252(2)</td>
<td>0.256(1)</td>
</tr>
<tr>
<td><strong>Reliability Factors</strong></td>
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<td></td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.566</td>
<td>2.359</td>
<td>2.147</td>
<td>2.398</td>
<td>2.196</td>
</tr>
<tr>
<td>wr$_p$</td>
<td>0.0729</td>
<td>0.0711</td>
<td>0.0670</td>
<td>0.0665</td>
<td>0.0642</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.0574</td>
<td>0.0551</td>
<td>0.0535</td>
<td>0.0516</td>
<td>0.0502</td>
</tr>
</tbody>
</table>

6.2.5 X-ray Photoelectron Spectroscopy (XPS)

XPS spectra were measured on a Kratos AXIS 165 spectrometer, equipped with a monochromatic Al K$_\alpha$ X-ray source (15 mA, 14 kV) and a hybrid lens with a spot size of 700 $\times$ 400 μm$^2$. The air-stable samples were finely ground, pressed into indium foil, mounted on a copper sample holder with carbon tape, and transferred in a sealed container to the analysis chamber of the spectrometer. The pressure inside the XPS instrument was maintained between $10^{-7}$ and $10^{-9}$ Pa. Samples were sputter-cleaned with
an Ar\textsuperscript{+} ion beam (4 kV, 10 mA) until no further changes were observed in the peak shoulders associated with surface oxides, which could not be completely removed. Core-line binding energies (BEs) were, within standard uncertainties, the same before and after the sputtering procedure. Survey spectra in the range of 0–1100 eV were collected with a pass energy of 160 eV, step size of 0.7 eV, and a sweep time of 180 s. These spectra revealed the presence of all expected elements, but the use of indium foil in the sample holder interfered with accurate determination of the composition of these Mn-substituted AgInSe\textsubscript{2} samples. However, it was clear that the Mn 2\textit{p} core-line peaks become relatively more intense as the level of Mn-substitution increases in these samples. High-resolution spectra (collected with pass energy of 20 eV, step size of 0.05 eV, and sweep time of 180 s) were measured in the appropriate BE ranges as determined from the survey scan for the Ag 3\textit{d}, In 3\textit{d}, Se 3\textit{d}, and Mn 2\textit{p} core lines. Charge neutralization was applied to all samples in varying degrees with the best settings chosen (charge balance of 1.8–3.6 V, filament current of 1.6–2.0 A) to give the most intense and sharpest peaks. The spectra were calibrated to the C 1\textit{s} line at 284.8 eV, arising from adventitious carbon and were analyzed with use of the CasaXPS software package.\textsuperscript{313} The background arising from energy loss was removed by applying a Shirley-type function and the peaks were fit to pseudo-Voigt (70\% Gaussian and 30\% Lorentzian) line profiles to take into account spectrometer and lifetime broadening effects. On the basis of many previous measurements made on this instrument, we estimate a precision of better than ±0.1 eV in the BEs.
6.2.6 Magnetic Measurements

Direct current magnetization studies were carried out using a superconducting quantum interference device magnetometer (Quantum Design MPMS-7). The temperature dependence of magnetization data was measured from 5 to 300 K under an applied field of 5 kOe under zero-field-cooling conditions. Approximately 30 mg of powder were packed in a capsule for magnetic measurements, and the magnetic susceptibility of the Mn-substituted samples was corrected for the diamagnetic contribution from the capsule and the parent, AgInSe$_2$, sample.

6.2.7 Optical Diffuse Reflectance UV/VIS/NIR Spectroscopy

A Varian Cary 5000 spectrometer, equipped with a Harrick Praying Mantis diffuse reflectance accessory, was used to collect the optical diffuse reflectance spectra of the AgInSe$_2$, Ag$_{1-2x}$Mn$_x$InSe$_2$ ($x$=0.015, 0.03, 0.05, 0.07, 0.10) and Ag$_{1-x}$Mn$_x$InSe$_2$ ($x$=0.05, 0.10, 0.15) compounds over the ultraviolet, visible, and near infrared spectral regimes (UV/VIS/NIR). Each sample was ground and placed in a sample holder to a depth of 3 mm. Barium sulfate (Fisher, 99.92%) was used as a 100% reflectance standard. The measurement was conducted at a scan rate of 600 nm/min. Using the Kubelka-Munk transformation, $\alpha_{KM} / s = (1-R)^2/(2R)$, the raw reflectance (R) was converted to a relative absorption ($\alpha_{KM}$) since the scattering coefficient, $s$, is unknown.$^{314}$ The Urbach energy was also obtained by fitting the optical data to the functional form $\alpha = A \cdot \exp(E - E_g/E_u)$, where A is a constant, E is the photon energy in eV, $E_g$ is the band gap energy, and $E_u$ is the Urbach energy.$^{315}$
6.2.8 Electronic Structure

6.2.8.1 WIEN2k

The crystal structure of AgInSe$_2$, determined by Benoit and coworkers via single crystal X-ray diffraction, was used for the electronic structure calculations.$^{310}$ The band structure and DOS were calculated for the parent compound AgInSe$_2$ using the WIEN2k package, which utilizes the full-potential linearized augmented plane-wave method (FLAPW) within density functional theory (DFT) for solving the Kohn-Sham equations for total energy.$^{316-318}$ The exchange and correlation effects were treated using the Perdew, Burke, and Ernzerhof generalized gradient approximation (PBE-GGA) and the modified Becke-Johnson (mBJ) potential.$^{319}$ The self-consistent field (SCF) calculation converged when the energy difference between successive iterations fell below 0.0001 Ry. Additionally, the geometry of the structure was optimized. A 3,000 k-point mesh was used in the full Brillouin zone (BZ), which corresponded to 240 k-points within the irreducible Brillouin zone (iBZ).

6.2.8.2 CASTEP

Electronic structure calculations were also carried out using the total-energy code of CASTEP, allowing for a quantitative bond analysis.$^{320,321}$ In CASTEP, the total energy is calculated using the plane-wave pseudopotential method of DFT. PBE-GGA was used to treat the exchange and correlation effects.$^{319}$ Using this method, the interactions between the ionic cores and the electrons are described by norm-conserving pseudopotentials.$^{322}$ The following orbital electrons were treated as valence electrons: Ag 5$s^2$4$p^6$4$d^9$, In 5$s^2$5$p^1$, and Se 4$s^2$4$p^4$. The number of plane-waves included in the basis
set was determined by a cutoff energy of 765 eV and the numerical integration of the Brillouin zone was performed using a $2 \times 2 \times 3$ Monkhorst-Pack k-point sampling. Default values of the CASTEP code were taken for the remaining parameters and convergence criteria. The bond orders were then calculated using a Mulliken bond population analysis within the CASTEP code.$^{323,324}$

6.3 Results and Discussion

6.3.1 Synthesis and Structural Characterization

6.3.1.1 Synthesis and Phase Identification

Initial attempts to incorporate manganese in AgInSe$_2$ were carried out with samples of the nominal stoichiometry AgIn$_{1-x}$Mn$_x$Se$_2$ ($x=0.025$-$0.10$). While XRPD patterns indicated that a chalcopyrite phase was the main product, significant amounts of a secondary phase, Ag$_2$Se, were identified.$^{325}$ Several heating profiles and annealing procedures were used in attempt to acquire phase-pure samples, but Ag$_2$Se was always present and the amount increased with increasing manganese content. These results prompted us to investigate substitutions of Mn on the Ag site rather than on the In site, which appears more favorable despite the different expected oxidation states of these cations.

Samples of the Ag$_{1-x}$Mn$_x$InSe$_2$ system ($x=0.05$-$0.15$) were therefore prepared and all of the diffraction peaks in the X-ray powder diffractogram of the Ag$_{0.95}$Mn$_{0.05}$InSe$_2$ sample could be indexed to the chalcopyrite structure. However, it should be noted that although no evidence of secondary phases was apparent, the existence of secondary phases below the detection limit of laboratory X-ray powder diffraction could be present.
in the sample. Although the diffraction patterns indicated that the chalcopyrite phase is the dominant product in the case of x=0.10 and 0.15, the presence of the secondary phase AgIn$_5$Se$_8$\cite{326,327} is indicative of a low solubility of manganese in the Ag$_{1-x}$Mn$_x$InSe$_2$ system. This is not surprising because the formula does not charge balance if manganese is assumed to be in a 2$^+$ oxidation state. In general, the chalcopyrite structure is flexible and can often exhibit a number of different defects to achieve charge balance; however, the maximum value of x is often found to be low.\cite{302,303} For the CuIn$_{1-x}$Mn$_x$Se$_2$\cite{302} and Cu$_{1-x}$Mn$_x$In$_2$\cite{303} systems, the maximum value of x that can be incorporated without secondary phases is 0.10, while the Cu$_{0.95-x}$Mn$_{0.05}$InSe$_2$ series has a maximum x value of 0.20 before secondary phases form.\cite{304} For the Ag$_{1-x}$Mn$_x$InSe$_2$ system, several attempts to gain further solubility of manganese using different heating profiles were unsuccessful. Quenching samples from high temperature did nothing to eliminate the secondary phase and resulted in peak broadening for the chalcopyrite phase. Annealing samples in which AgIn$_5$Se$_8$ was identified often reduced secondary phase presence, but never eliminated it.

In order to pursue phase-pure silver-deficient, Mn-substituted samples with a charge-balanced composition, reactions to prepare Ag$_{1-2x}$Mn$_x$InSe$_2$ were carried out. Careful analyses of XRPD data showed that phase-pure samples of Ag$_{1-2x}$Mn$_x$InSe$_2$ (x=0.015-0.07) could be reliably prepared with no evidence of AgSe$_2$ and/or AgIn$_5$Se$_8$; however when x reaches 0.10, the diffraction peaks of AgIn$_5$Se$_8$ are become barely visible. In the Ag$_{1-2x}$Mn$_x$InSe$_2$ formula, the replacement of Mn$^{2+}$ for Ag$^{+}$ is charge compensated by the presence of Ag site vacancies. In order to support the composition of these materials from XRPD data, Rietveld refinements were carried out.
6.3.1.2 Rietveld Refinement and Structure Analysis

Rietveld refinements were carried out using X-ray powder diffraction data obtained for the parent AgInSe$_2$ and for all phase-pure Mn-substituted materials, Ag$_{1-x}$Mn$_x$InSe$_2$ (x=0.05), and Ag$_{1-2x}$Mn$_x$InSe$_2$ (x=0.015-0.07). The Rietveld refinements were performed in order to investigate the general effects that the manganese incorporation has on the chalcopyrite crystal lattice. Since the site occupation factors in the substituted materials were constrained to those of the nominal composition during Rietveld refinements, EDS spectra were collected for support of the composition.

In the chalcopyrite-type structure, there are three crystallographically unique sites; 4a (0, 0, 0), 4b (0, 0, 0.5), and 8d (x, 0.25, 0.0125) where x is near 0.25. For the pristine AgInSe$_2$ compound, Ag, In, and Se, occupy the 4a, 4b, and 8d sites, respectively. The SOFs for all three ions were freely refined in the parent compound, revealing that the 4a and 8d sites are likely deficient, where SOF$_{Ag}$=0.95(1) and SOF$_{Se}$=0.984(6), respectively. Deficiencies on the 4a and 8d sites are not uncommon for related chalcopyrites.$^{328-331}$

Using EDS, the chemical composition of the parent compound was found to be Ag$_{0.92}$In$_{1.00}$Se$_{1.90}$, supporting the results found by Rietveld analysis. Additionally, similar deficiencies were found in AgInS$_2$, AgGaSe$_2$, AgGa$_{0.9}$In$_{0.1}$Se$_2$, and AgGa$_{0.8}$In$_{0.2}$Se$_2$ using electron probe microanalysis or EDS.$^{328-331}$ The lattice parameters of AgInSe$_2$ were refined to a=6.1040(2) Å and c=11.7116(5) Å using the Rietveld method. These values are similar to those found in the literature, a=6.09-6.104 Å and c=11.65-11.714 Å.$^{291,310,332-334}$ The volume of the cell was found to be 436.35(2) Å$^3$, which is within the range of 432.08-436.45 Å$^3$ that was reported in previous works.$^{291,310,332-334}$
Figure 6.1. The Rietveld refinement results of Ag\textsubscript{1-x}Mn\textsubscript{x}InSe\textsubscript{2} (x=0.05) using X-ray powder diffraction data. In the plot, the observed data (+) and the calculated data (solid line) are shown on top. Below these data are two rows of tick marks (ǀ) corresponding to the locations of the expected Bragg reflections of AgInSe\textsubscript{2} (top) and Si (bottom). The difference between the observed and the calculated data (solid line) is shown at the bottom of the plot.

In the case of Ag\textsubscript{1-x}Mn\textsubscript{x}InSe\textsubscript{2} (x=0.05), a satisfactory model could only be obtained when manganese was placed on the 4a site. Due to the data being laboratory X-ray powder diffraction data, all site occupation factors were constrained to the nominal composition. The use of the nominal composition is supported by EDS analysis, where
the formula was found to be Ag$_{0.87}$Mn$_{0.05}$In$_{1.00}$Se$_{1.90}$. The observed decrease of the lattice parameters in Ag$_{1-x}$Mn$_x$InSe$_2$ (x=0.05), compared to the parent, was expected due to the crystal radius of four-coordinate Mn$^{2+}$ being smaller than that of four-coordinate Ag$^+$, 0.80 Å versus 1.14 Å, respectively.$^{335}$ It should be noted, however, that due to Ag$^+$ having similar X-ray scattering factors with In$^{3+}$, we cannot determine the existence of Ag$_{\text{In}}$ or In$_{\text{Ag}}$ anti-site occupation, which are typical defects for chalcopyrite-type materials.$^{336,337}$ The Rietveld refinement of the Ag$_{0.95}$Mn$_{0.05}$InSe$_2$ compound resulted in a $\chi^2$ value of 1.801 and a relatively flat difference plot.

**Table 6.2. Formulae calculated for the Ag$_{1-2x}$Mn$_x$InSe$_2$ (x=0.015-0.07) series using EDS data.**

<table>
<thead>
<tr>
<th>Mn content, x</th>
<th>Formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>Ag$<em>{0.947(3)}$Mn$</em>{0.018(5)}$In$<em>{1.000(3)}$Se$</em>{1.903(3)}$</td>
</tr>
<tr>
<td>0.03</td>
<td>Ag$<em>{0.916(3)}$Mn$</em>{0.026(4)}$In$<em>{1.000(3)}$Se$</em>{1.877(3)}$</td>
</tr>
<tr>
<td>0.05</td>
<td>Ag$<em>{0.871(3)}$Mn$</em>{0.048(4)}$In$<em>{1.000(3)}$Se$</em>{1.900(3)}$</td>
</tr>
<tr>
<td>0.07</td>
<td>Ag$<em>{0.781(4)}$Mn$</em>{0.062(4)}$In$<em>{1.000(4)}$Se$</em>{1.780(4)}$</td>
</tr>
</tbody>
</table>

As in the case of Ag$_{0.95}$Mn$_{0.5}$InSe$_2$, satisfactory refinements for the Ag$_{1-2x}$Mn$_x$InSe$_2$ series were only obtained if manganese was placed on the 4a site. All refinements converged with a $\chi^2$ of ~2; the results for x=0.05 are graphically shown in Figure 6.1 as a representative of the series. Across the Ag$_{1-2x}$Mn$_x$InSe$_2$ series, the EDS data support decreasing silver content with increasing manganese. Additionally, the manganese content found by EDS is relatively close to that in the intended formula, Table 6.2. The refined cell parameters, $a$ and $c$, and overall unit cell volume, $V$, in the Ag$_{1-2x}$Mn$_x$InSe$_2$ series were found to decrease as expected, since one smaller divalent
manganese cation replaces two larger monovalent silver cations (Figure 6.2). The decrease was observed to be linear with the addition of manganese, in accordance with Vegard’s law, thus suggesting that manganese has a continuously variable content on the 4a site.\textsuperscript{338}

Figure 6.2. Lattice parameters and volume versus the manganese content (x) of Ag\textsubscript{1-2x}Mn\textsubscript{x}InSe\textsubscript{2} (x=0-0.07). Linear fits to the data are shown. Data error bars are smaller than the markers.
Figure 6.3. The doubling of the zinc blende unit cell creates an ideal chalcopyrite lattice where the bond distances, I-VI and III-VI would be equivalent, the anion x-coordinate would be exactly 0.25 and the ratio of the lattice parameters, c/a, would be 2. In AgInSe$_2$, the Ag-Se bond distance is greater than the In-Se bond distance making the selenium x-coordinate less than 0.25 and the c/a ratio less than 2.

The chalcopyrite structure is an ordered superstructure of the cubic zinc blende structure, where one of the axes is approximately doubled relative to the subcell. The tetragonal distortion in chalcopyrites can be determined from the ratio of the lattice parameters, c/a (Figure 6.3). When the value is closer to 2, there is less distortion resulting from the difference between the bond distances of the anion and the two cations. For the parent compound and Ag$_{0.95}$Mn$_{0.05}$InSe$_2$, the c/a ratio was found to be 1.919,
which is identical to that reported by Grzeta-Plenkovic et al.\textsuperscript{332} For the Ag\textsubscript{1-2x}Mn\textsubscript{x}InSe\textsubscript{2} series, the $c/a$ ratio increased with increasing manganese concentration, indicating decreasing tetrahedral distortion. Although the increase in the $c/a$ ratio is only 0.36\% across the series, the trend is clearly linear (Figure 6.4). The systematic evolution of multiple crystallographic parameters with Mn content provides very strong evidence for the formation of a true solid solution in this system.

![Graph showing the ratio of the lattice parameters ($c/a$) versus the manganese content ($x$).](image)

**Figure 6.4.** The ratio of the lattice parameters ($c/a$) versus the manganese content ($x$). The linear fit to the data for $x=0$-0.07 in the series Ag\textsubscript{1-2x}In\textsubscript{x}MnSe\textsubscript{2} is shown. Data error bars are smaller than the markers.

6.3.2 XPS analysis

XPS spectra were analyzed to obtain information about the oxidation states of the elemental components in the AgInSe\textsubscript{2} samples and to examine the effect of Mn substitution on the core-level BEs, in analogy to similar studies on CuInS\textsubscript{2} and
The Mn 2p, Ag 3d, In 3d, and Se 3d core-line XPS spectra are shown in Figure 6.4, and measured BEs are listed in Table 6.3.

Figure 6.5. (a) Mn 2p$_{3/2}$, (b) Ag 3d, (c) In 3d, and (d) Se 3d XPS spectra for Mn-doped AgInSe$_2$ samples. In (a), the components marked A–C are discussed in the text.
Table 6.3. Core-line BEs (eV) for Mn-doped AgInSe$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn 2p$_{3/2}^a$</th>
<th>Ag 3d$_{5/2}$</th>
<th>In 3d$_{5/2}$</th>
<th>Se 3d$_{5/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgInSe$_2$</td>
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<td>368.1</td>
<td>444.9</td>
<td>54.2</td>
</tr>
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<td>Ag$<em>{0.94}$Mn$</em>{0.03}$InSe$_2$</td>
<td>641.4, 640.2, 644.3</td>
<td>368.2</td>
<td>444.9</td>
<td>54.2</td>
</tr>
<tr>
<td>Ag$<em>{0.90}$Mn$</em>{0.05}$InSe$_2$</td>
<td>641.3, 640.3, 644.0</td>
<td>368.2</td>
<td>444.9</td>
<td>54.3</td>
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<tr>
<td>Ag$<em>{0.86}$Mn$</em>{0.07}$InSe$_2$</td>
<td>641.2, 640.3, 644.2</td>
<td>368.2</td>
<td>444.9</td>
<td>54.3</td>
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<td>368.2</td>
<td>444.9</td>
<td>54.3</td>
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<tr>
<td>Ag$<em>{0.90}$Mn$</em>{0.10}$InSe$_2$</td>
<td>641.2, 640.2, 644.2</td>
<td>368.1</td>
<td>445.0</td>
<td>54.3</td>
</tr>
<tr>
<td>Ag$<em>{0.85}$Mn$</em>{0.15}$InSe$_2$</td>
<td>641.2, 640.3, 644.1</td>
<td>368.1</td>
<td>444.9</td>
<td>54.3</td>
</tr>
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</table>

The Mn 2p$_{3/2}$ core-line peak was barely detectable above background at the lowest Mn substitution levels (Ag$_{1-2x}$Mn$_x$InSe$_2$ ($x=0.03$)), but its presence became indisputable with greater Mn concentration (Ag$_{1-x}$Mn$_x$InSe$_2$ ($x=0.15$), shown in Figure 6.5a. The peak profile resembles that seen in Mn-substituted CuInS$_2$ and CuInSe$_2$,\textsuperscript{303,339} as well as binary manganese chalcogenides (MnSe, MnTe).\textsuperscript{340,341} This peak was fit to three components: (A) the main core-line peak, (B) a weak shoulder at lower BE, corresponding to a reduced Mn species caused by the Ar$^+$ sputtering procedure, and (C) a broad satellite at higher BE resulting from a metal-to-ligand shakeup process.\textsuperscript{342} We do not regard the slightly higher Mn 2p$_{3/2}$ BE values (641.4 eV) found in Ag$_{1-2x}$Mn$_x$InSe$_2$ ($x=0.03$), to be a meaningful shift; it is difficult to locate the peak maximum because the signal is very weak and difficult to distinguish from background. For all remaining samples, the Mn 2p$_{3/2}$ BE (641.2–641.3 eV) is identical to that in Mn-doped CuInSe$_2$ (641.2–641.3 eV)\textsuperscript{339} and slightly lower than in Mn-substituted CuInS$_2$ (641.5–641.6 eV)\textsuperscript{303}. These BEs were significantly higher than in elemental Mn (639.7(8) eV),
indicating the presence of cationic species, and were comparable to that in MnO (641.2(5) eV), supporting the assignment of Mn$^{2+}$.

The Ag 3$d$ spectra, consisting of spin-orbit-split 3$d_{5/2}$ and 3$d_{3/2}$ peaks, did not change upon any level of substitution of Mn into AgInSe$_2$; the Ag 3$d_{5/2}$ BE remained invariant at 368.1–368.2 eV (Figure 6.5b). Although monovalent Ag is anticipated in these samples, BE shift correlations could not be applied here in a straightforward manner to determine oxidation states because Ag 3$d$ spectra are subject to severe final-state effects. For example, the Ag 3$d_{5/2}$ BE was actually lower in AgO (367.4(1) eV), which contains nominal Ag$^+$ and Ag$^{3+}$ species, than in Ag metal (368.2(1) eV), contrary to the naïve expectation that more positively charged species should lead to higher BEs. The NIST database indicates that Ag 3$d_{5/2}$ BE values for compounds containing monovalent Ag (ranging from 367.7 to 368.4 eV, with an average of 368.0 eV) tend to be slightly lower than in Ag metal (ranging from 367.9 to 368.4 eV, with an average of 368.2 eV). Close inspection of the spectra for Mn-substituted AgInSe$_2$ revealed a slight asymmetry of the peak shape to higher BE. However, it was inconclusive whether this asymmetry originated from a reduced Ag$^0$ species caused by Ar$^+$ sputtering or from Doniach-Šunjić broadening effects. Perhaps the best diagnostic feature to examine is the full-width-at-half-maximum (FWHM) of the Ag 3$d_{5/2}$ core-line peak, which tends to be wider for Ag$^+$ (0.8–1.1 eV) than for Ag$^0$ (0.4–0.6 eV).

The similarity of the FWHM values in the Mn-substituted AgInSe$_2$ samples (0.8–1.1 eV) to those in other Ag$^+$-containing compounds lends confidence to the assignment of monovalent Ag. Additionally, similar results were found for AgInSe$_2$ prepared as nanorods from single source precursors and hydrothermal synthesis. Although no charge
shift correction was specified in either case, these materials have been reported to display a Ag 3d\textsubscript{5/2} BE of 367.6 and 367.2 eV, respectively.\textsuperscript{351,352}

The In 3d spectra (Figure 6.5c) revealed that the In 3d\textsubscript{5/2} BEs (444.9–445.0 eV) match with that in In\textsubscript{2}O\textsubscript{3} (444.8(4) eV),\textsuperscript{342} consistent with the assignment of In\textsuperscript{3+}. These results were identical to those found for the Mn-substituted CuInSe\textsubscript{2} materials and similar to the BE of 445.3 eV reported for the In 3d\textsubscript{5/2} in the iron-substituted CuInS\textsubscript{2}.\textsuperscript{339,301} AgInSe\textsubscript{2} nanorods display BEs near those reported here at 444.0 and 444.4 eV.\textsuperscript{351,352}

The Se 3d spectra (Figure 6.5d) showed a broad signal fitted to two 3d\textsubscript{3/2} and 3d\textsubscript{5/2} components; the Se 3d\textsubscript{5/2} BEs (54.2–54.3 eV) were identical to those in Mn-substituted CuInSe\textsubscript{2}\textsuperscript{339} and lower than in elemental Se (55.3(5) eV),\textsuperscript{342} confirming the presence of anionic selenium. In summary, the introduction of Mn\textsuperscript{2+} into AgInSe\textsubscript{2} had negligible effect on the core-line peaks of the other component elements, suggesting little change in their local electronic structure.

6.3.3 Magnetism

Since XPS confirmed the presence of divalent manganese, magnetic measurements of the samples were carried out in order to investigate any effect that the incorporation of divalent manganese had on magnetic properties. The magnetization of the Ag\textsubscript{1-2x}Mn\textsubscript{x}InSe\textsubscript{2} (x=0.5 and 0.07) samples was investigated with an applied field of 5 kOe. The plot of magnetization as a function of temperature for these materials clearly shows paramagnetic behavior with no magnetic transition down to 5 K. At low temperature, the samples exhibit a sharp upturn, which has also been observed for other substituted chalcopyrite materials such as CuIn\textsubscript{1-x}Mn\textsubscript{x}Se\textsubscript{2}, Cu\textsubscript{1-y}In\textsubscript{1+y}Mn\textsubscript{2y}Se\textsubscript{2}, CuIn\textsubscript{1-x}Mn\textsubscript{x}S\textsubscript{2}, and Cu\textsubscript{1-y}Mn\textsubscript{y}InS\textsubscript{2}.\textsuperscript{302,303} It has been proposed that this upturn is due to the
presence of bound or trapped carriers in the materials. The data for $x=0.07$ are shown in Figure 6.6 (Top) as representative data.

![Graph of magnetization vs temperature for Ag$_{1-2x}$Mn$_x$InSe$_2$](image)

Figure 6.6. (Top) Temperature dependence of the magnetization of Ag$_{1-2x}$Mn$_x$InSe$_2$ ($x=0.07$). (Bottom) The inverse of magnetic susceptibility ($1/\chi$) as a function of temperature of Ag$_{1-2x}$Mn$_x$InSe$_2$ ($x=0.07$). The solid line is a fit ($T>65$K) using the Curie-Weiss law.

The temperature dependence of the inverse magnetic susceptibility was examined and the molar magnetic susceptibility was found to obey the Curie-Weiss law above 65 K. Therefore, the magnetic moments as well as the Weiss temperatures ($\theta$) were calculated using the Curie-Weiss law for $T>65$K. In the case of $x=0.05$, $\theta$ was found to be -20.6 K indicating weak antiferromagnetic interactions in the sample, while that of the $x=0.07$ sample was calculated to be -15.8 K (Figure 6.6, Bottom), demonstrating that the
additional incorporation of manganese (and vacancies) barely modifies the antiferromagnetic coupling. The calculated magnetic moments of 5.80 and 5.20 μB are close to the theoretical value of 5.9 μB expected for the Mn²⁺ free ion. These results further support the presence of divalent Mn as suggested by XPS.

6.3.4 Optical Diffuse Reflectance UV/Vis/NIR Spectroscopy

For other related transition metal substituted chalcopyrite-type materials, it has been shown that the substituent can have either a negligible or marked effect on the optical absorption edge. Therefore, optical diffuse reflectance data were collected for all of the Mn-substituted samples as well as the parent compound to determine what effect, if any, the addition of manganese into the compounds would have on the optical properties. All spectra exhibit a relatively sharp absorption edge in the vicinity of 1.2 eV. For the Ag₁₋ₓMnₓInSe₂ (x=0.05-0.15) series, the absorption edges overlapped. However, in the Ag₁₋₂ₓMnₓInSe₂ (x=0.015-0.07) series, the absorption edge clearly shifts as a function of manganese content (Figure 6.7).
The optical diffuse reflectance spectra for the Ag$_{1-2x}$Mn$_x$InSe$_2$ series.

Optical absorption edges commonly exhibit a diffuse tail that originates from defects within the crystal structure that induce defect states within the band structure. These defect states occur at the top of the valence and the bottom of the conduction bands, creating a smearing of the band edge known as the Urbach tail which can be clearly seen at energies just below the band gap.\textsuperscript{354,355} This tail should be considered when analyzing the band gap energy of a semiconductor, as it allows the sample homogeneity to be assessed and provides a lower bound for the band gap energy.\textsuperscript{356} The Urbach tail appears linear when the logarithm of absorption is plotted against photon energy, and the sample inhomogeneity can be assessed by quantitatively fitting the slope of this line to extract the magnitude of the broadening, commonly referred to as the Urbach energy.\textsuperscript{315} Across the Ag$_{1-2x}$Mn$_x$InSe$_2$ series, the Urbach energy is expected to
increase with increasing $x$, as the amount of substitutional defects (manganese and vacancies) in the crystal lattice increases.\textsuperscript{357} By fitting the data, it was found that the Urbach energy generally falls within the range of 0.045–0.052 eV for the series (Figure 6.8a), and is therefore only slightly modified over the achieved range of Mn-substitution. Somewhat surprisingly, the Urbach energy generally decreases with increasing manganese content. This could reflect a small increase in the sample homogeneity due to the introduction of Mn, which may lower the phase melting point and therefore facilitate more rapid equilibration. When plotting the natural log of absorption as a function of energy, Kumar and Pradeep\textsuperscript{358} determined from the slope an Urbach energy of 0.166 eV for AgInSe\textsubscript{2}. Converting this value to the log-base-ten scale, the Urbach energy was found to be 0.072 eV, slightly higher than in the present samples. This difference is likely due to the variations in sample preparation method. Kumar and Pradeep\textsuperscript{358} prepared the sample via vacuum evaporation on a glass substrate at high temperature in contrast to the present solid-state synthesis.
Figure 6.8. Optical diffuse reflectance spectra data of (top) AgInSe$_2$ and (bottom) Ag$_{1-2x}$Mn$_x$InSe$_2$ (x=0.07) with Kubelka-Munk derived (a) log of the absorption as a function of energy with an overlaid fit used to determine the Urbach energy ($E_u$), (b) the square of the absorption as a function of energy (direct band gap function), where the lighter region shows the linear portion of the curve, (c) the square root of the absorption as a function of energy (indirect band gap function), where the lighter region shows the linear portion of the curve, and (d) relative absorbance as a function of energy where the dotted curve shows the fitting used to estimate the band gap energy ($E_g$).

In semiconductor materials, a relatively sharp absorption edge is indicative of a direct band gap material, while a more gradual onset designates a band gap of indirect character.$^{354}$ To determine the nature of the band gap, the absorption data, excluding the previously found Urbach tail region, were fitted to the function for a direct gap semiconductor, $\alpha = A \cdot (E-E_g)^{1/2}/E$, and to the function for an indirect semiconductor, $\alpha = A \cdot (E-E_g)^2/E$, where $A$ is a constant, $E$ is the photon energy in eV, and $E_g$ is the band gap energy.$^{354}$ Both the square of the absorption (Figure 6.8b) and the square root of the absorption (Figure 6.8c) were plotted as a function of energy and the data were fitted to
the direct and indirect functions, respectively. Based on these fits, it was found that all of the compounds within the $\text{Ag}_{1-2x}\text{Mn}_x\text{InSe}_2$ ($x=0-0.07$) series had a larger range of linearity using the direct function rather than the indirect function, and thus all compounds within the series were judged to have direct band gaps. Therefore, the reported optical band gaps were determined using the direct gap functional form.

Intriguingly, the parent compound, $\text{AgInSe}_2$, has an optical response which is characteristic of not one but two direct optical transitions, with energies of 1.21 and 1.25 eV (Figure 6.8d). For the manganese-substituted compounds, $\text{Ag}_{1-2x}\text{Mn}_x\text{InSe}_2$ ($x=0.015-0.07$), the dual transitions could not be resolved and band gaps were instead determined from fits of single direct excitations, and thus appear slightly offset (about 0.01 eV lower) in comparison to the pristine compound (Figure 6.8d). The derived band gap gradually increased from 1.19 to 1.23 eV with increasing Mn substitution (Figure 6.9). In order to better understand the origin of the band gap, in the $\text{Ag}_{1-2x}\text{Mn}_x\text{InSe}_2$ series, and the presence of the two transitions in the optical absorption edge for the parent compound, electronic structure calculations were carried out.
Figure 6.9. The estimated band gap and Urbach energies versus the manganese content (x) of Ag$_{1-2x}$Mn$_x$InSe$_2$. Data error bars are smaller than the markers.

6.3.5 Electronic Structure

Jaffe and Zunger were the first to report the electronic structures of chalcopyrite-type compounds within the formulism of DFT. In this early work, a potential-variation mixed-basis (PVMB) approach was used to study chemical trends for the compounds, CuAlVI$_2$, CuGaVI$_2$, and CuInVI$_2$, where VI was either sulfur or selenium.\textsuperscript{359} Additionally, electronic structure calculations for several other chalcopyrite type compounds have been previously reported in the literature.\textsuperscript{359-362} These calculations are generally in agreement that the chalcopyrite materials are direct-band-gap semiconductors, where the top of the valence band is dominated by the antibonding hybridization of the Cu or Ag $d$-orbitals with the chalcogen $p$-orbitals.\textsuperscript{291,359,364} The band structure of AgInSe$_2$ specifically has been calculated by Rashkeev and Lambrecht.\textsuperscript{360}
Ozaki and Adachi,\textsuperscript{361} and Maeda and coworkers.\textsuperscript{362} The 0.10 eV direct band gap calculated by Rashkeev and Lambrecht\textsuperscript{360} was determined using a local density approximation (LDA) within DFT, which is known to severely underestimate the band gaps of semiconductors.\textsuperscript{363} In the work of Ozaki and Adachi,\textsuperscript{360} as well as that of Maeda et al.,\textsuperscript{362} a pseudopotential method was used. While providing more accurate band gap energies, these pseudopotential methods can be generally inaccurate in their description of the partial DOS in the valence region, below the Fermi level. For these reasons, we chose to recalculate the electronic structure of AgInSe\textsubscript{2} using the FLAPW method within DFT, combined with the PBE-GGA and the application of the mBJ potential.

The calculated band structure of AgInSe\textsubscript{2} is plotted in Figure 6.10 (left). It is clear that AgInSe\textsubscript{2} is a direct-band-gap semiconductor with a band gap of 0.95 eV at the Γ-point. The next lowest energy transition of 1.13 eV also occurs at the Γ-point at the intersection of two bands. Therefore, it is likely that the two absorption edges in the optical spectrum that were fit using the direct band gap function are due to these two transitions. The calculated band gap is a little smaller than the experimental values, but the results are much closer in agreement compared to some previously reported in the literature.\textsuperscript{360,362} Previously reported calculations indicate a direct band gap for AgInSe\textsubscript{2} at the Γ-point\textsuperscript{360-362}; however, with the exception of the work by Maeda et al.\textsuperscript{362} previous works did not discuss the DOS.
Figure 6.10. (Left) Calculated electronic band structure of AgInSe$_2$. (Right) Total and partial density of states (DOS) for AgInSe$_2$. The dotted line denotes the Fermi level ($E_F$).

To better understand the origin of the band gap in AgInSe$_2$, the total and partial DOS were calculated, shown in Figure 6.10 (right). The valence band region from -7 to -5 eV principally originates from Se-4$p$ and In-5$s$ orbitals, with minor contributions from the Ag-4$d$ and Se-4$s$ orbitals. Approaching the top of the valence band, -5 to -2 eV, the DOS are primarily comprised of the Ag-4$d$ and Se-4$p$ states, with lesser participation from the In-5$p$ states. The states in the highest energy valence band region, closest to the Fermi level ($E_F$), -2 to 0 eV, evolve predominantly from Se-4$p$ and Ag-4$d$ orbitals. On the other side of the band gap, the minimum states in the conduction band (from +1 to +3.5 eV) chiefly arise from the Se-4$s$, Se-4$p$, and In-5$s$ orbitals. Higher in the conduction band, +3.5 to +6 eV, the states are largely due to the Ag-4$s$ and In-5$p$ orbitals along with
the Se-4s and Se-4p orbitals. Based on these calculations, it can be surmised that the lowest energy direct band gap excitation observed in the optical spectrum in Figure 6.7 arises primarily from the strongly hybridized Ag-4d/Se-4p states to the In-5s orbitals.

Considering the large contribution of the Ag-4d orbitals near the Fermi level, it is possible that as manganese is added to the material, and silver is thus removed, the band gap might change. In fact, it has been shown that the Ag-4d-Se4p interaction is an antibonding hybridization that is responsible for the band gap anomaly observed for chalcopyrite materials, meaning that the band gaps of the chalcopyrites are considerably smaller than one would expect based on the binary analogs. However, in the Ag1-xMnxInSe2 series, no change is observed in the experimental band gaps. This is similar to the results found in the CuInSe2 system for the CuIn1-xMnxSe2 and Cu1-yIn1-yMn2ySe2 series.302 Alternatively, in the case of Ag1-2xMnxInSe2, a small widening of the band gap is observed that may be due to the removal of Ag-d states at the Fermi level and a narrowing of the bands. On the other hand, the Burstein-Moss effect has been used to explain the band gap shift in several related, heavily-substituted chalcopyrites.365,366 A small increase in band gap with increasing vacancies on the 4a site has also been reported in the copper deficient CuInSe2 materials, Cu0.95-xMnxInSe2, where x=0-0.20.304

Similar calculations carried out using the CASTEP code provided semi-empirical population analyses, which allow for a more quantitative bond assessment. The calculated bond orders of In-Se and Ag-Se bonds are 0.23 e, and 0.34 e (covalent single-bond order is generally 1.0 e), respectively. It was found that the covalent nature of the Ag–Se bond is stronger than that of the In–Se bond. This result is expected based on the
higher degree of orbital overlap between Ag and Se that is evident in the partial DOS plot (Figure 6.10, (right)).

6.4 Conclusions

By experimenting with different stoichiometries and heating profiles, it was realized that $\text{Ag}_{1-x}\text{Mn}_x\text{InSe}_2 (x=0.05)$, and $\text{Ag}_{1-2x}\text{Mn}_x\text{InSe}_2 (x=0.015-0.07)$ materials could be prepared as phase-pure materials via high-temperature, solid-state synthesis. Using Rietveld analysis, the samples were found to be phase-pure and manganese was found to occupy the Ag (4a) site in the chalcopyrite lattice. Semi-quantitative analysis of the elements by EDS revealed that the actual Mn-In-Se compositions in the materials are close to the nominal compositions, while the silver amounts may be slightly deficient. Both XPS and magnetic measurements support the presence of divalent Mn.

Incorporation of Mn$^{2+}$ into the 4a site of the Ag-deficient AgInSe$_2$ chalcopyrite did not result in desirable (for spintronic applications) ferromagnetic interactions, and instead gave only weak antiferromagnetically coupled spins. However, the successful preparation of these materials gives rise to the idea that other transition metals may be used as substituents and could potentially result in ferromagnetic coupling. As the manganese content (and vacancy content) is increased in the $\text{Ag}_{1-2x}\text{Mn}_x\text{InSe}_2 (x=0.015-0.07)$ series, the degree of tetragonal distortion decreases, the band gaps slightly increase from 1.19 to 1.23 eV and the Urbach tail energy decreases. Careful fitting of the absorption edge data shows that all Mn-substituted materials are direct band gap semiconductors, as is the parent compound, thus these materials may be attractive for use in photovoltaic devices. The incorporation of manganese provides a simple means for
physical property tuning in this system, and likely represents a general mechanism for the substitution of silver ions with higher valence dopants.

6.5 References


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7. Conclusion

7.1 Restatement of Purpose

The focus of this dissertation was the in-depth study of the crystal structure, electronic structure, and physicochemical properties of $\alpha$-Cu$_2$ZnSiS$_4$, $\beta$-Cu$_2$ZnSiS$_4$, Cu$_2$CdSiS$_4$, Cu$_2$CdSnS$_4$, and AgInSe$_2$. As described in Chapter 1, the existence of all these compounds except $\beta$-Cu$_2$ZnSiS$_4$ had been known for many years. While these materials have had the synthetic procedures, lattice parameters, and some physicochemical properties previously reported in the literature, there was much remaining to be investigated. Each material still required more in-depth characterizations to discover its full potential as well as to correlate the crystal structure, electronic structure, and physicochemical properties. In this conclusion chapter the major findings of this dissertation will be highlighted. The work from Chapters 2, 3, and 5 will be grouped together, while the work featured in Chapters 4 and 6 will be discussed individually. Next, the overall broader impacts of these studies will be described. Finally, future directions will be delineated.

7.2 Major Findings of Chapters 2, 3, and 5

The work in Chapters 2, 3, and 5 focused on $\alpha$-Cu$_2$ZnSiS$_4$, $\beta$-Cu$_2$ZnSiS$_4$, and Cu$_2$CdSiS$_4$. Chapter 1 describes the single crystal X-ray structure solution and refinement for the wurtz-stannite ($Pmn2_1$) structured $\alpha$-Cu$_2$ZnSiS$_4$. It is amazing that a material originally discovery in 1967 did not have its crystal structure definitively determined (space group and atomic coordinates) until 2011. A year later, the Cu$_2$ZnSiS$_4$ composition was found to crystallize in two space groups, meaning that there are two
polymorphs of this material, α-Cu$_2$ZnSiS$_4$ and β-Cu$_2$ZnSiS$_4$. Considering that all previous reports on Cu$_2$ZnSiS$_4$ up until 2012$^{35-379,396-398}$ referred only to the wurtz-stannite structure it was surprising, and even startling, that 45 years after the discovery of the compound the second polymorph was revealed. α-Cu$_2$ZnSiS$_4$ and β-Cu$_2$ZnSiS$_4$ crystallize in space groups P$_{mn2_1}$ and P$_n$, respectively, and differ only in cation ordering.$^{399}$ The differences in the cation ordering result in X-ray powder diffraction patterns that vary by only small changes in peak intensities and a few additional weak peaks. The discovery of the new polymorph only occurred because of the Rietveld refinement of high-resolution synchrotron X-ray powder diffraction data using GSAS/EXPGUI. It was determined that the collected synchrotron diffraction data could only be modeled using both phases, leading to the conclusion that there are two polymorphs of the compound, α-Cu$_2$ZnSiS$_4$ (P$_{mn2_1}$) and β-Cu$_2$ZnSiS$_4$ (P$_n$).$^{399}$ Although the two structures differ only in cation ordering and the structural differences in terms of bond distances and angles are extremely subtle, their calculated electronic structures were found to vary. Both were found to be direct bandgap semiconductors at the Γ-point.$^{399,400}$ However, β-Cu$_2$ZnSiS$_4$ was found to have a markedly larger bandgap energy than α-Cu$_2$ZnSiS$_4$.$^{399,400}$ The total energy was calculated to be -27972.64989 Ry for α-Cu$_2$ZnSiS$_4$ and -27972.65612 Ry for β-Cu$_2$ZnSiS$_4$, thus, due to their similar ground state energies, the synthesis of each polymorph as a phase-pure material is a challenging endeavor that was not tackled in this work.

X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation states of the ions in α/β-Cu$_2$ZnSiS$_4$ and Cu$_2$CdSiS$_4$ single crystals. Critical analysis of the XPS spectra provided insight to the nature of the metal-sulfur bonding. In the course of
comparing $\alpha/\beta$-$\text{Cu}_2\text{ZnSiS}_4$ and $\text{Cu}_2\text{CdSiS}_4$ to similar silicon-containing materials in the literature, it was observed that XPS data of silicon sulfides is severely lacking, thus the comparison was extended to $\text{SiO}_2$ and $\text{SiO}_x$, where binding energies for the latter (Si-O) were found to be in the range of those (Si-S) in $\alpha/\beta$-$\text{Cu}_2\text{ZnSiS}_4$ and $\text{Cu}_2\text{CdSiS}_4$. Most metal-sulfides and zinc sulfides had BEs slightly higher than those found for the M-S bonds in $\alpha/\beta$-$\text{Cu}_2\text{ZnSiS}_4$ and $\text{Cu}_2\text{CdSiS}_4$ indicating that the M-S bonds in the title compounds are somewhat more covalent. Electronic structure calculations were also performed to further study the nature of the metal-sulfur bonding. Mulliken bond population analyses for these compounds calculated the bond orders in the ionic-covalent range.

7.3 Major Findings of Chapter 4

Chapter 4 focused on the study of $\text{Cu}_2\text{CdSnS}_4$ and further characterization of $\alpha$-$\text{Cu}_2\text{ZnSiS}_4$ and $\beta$-$\text{Cu}_2\text{ZnSiS}_4$. Remarkably $\text{Cu}_2\text{CdSnS}_4$, a synthetic relative of the mineral cernyite, first discovered in 1967, did not have its structure definitively determined (space group and atomic coordinates) until 2014. Using single crystal X-ray diffraction data the compound was found to crystallize with the stannite structure, in the noncentrosymmetric space group I-42$m$. In this instance, synchrotron X-ray powder diffraction data could only be modeled with one structure for the polycrystalline sample. Here the Rietveld refinement of high-resolution synchrotron X-ray powder diffraction data was also used to determine the sample purity, where all observed Bragg reflections matched those predicted for the model of $\text{Cu}_2\text{CdSnS}_4$, except for one weak peak that was not evident using laboratory X-ray powder diffraction. Because the challenge of synthesizing as $\alpha$-$\text{Cu}_2\text{ZnSiS}_4$ and $\beta$-$\text{Cu}_2\text{ZnSiS}_4$ as two phase-pure materials was not
overcome, the phases were further studied as a mixture and high-resolution synchrotron X-ray powder diffraction data were used to determine the weight fractions within the sample (~60/40).400

Cu$_2$CdSn$_4$ and α/β-Cu$_2$ZnSiS$_4$ were found to meet several important criteria for ideal nonlinear optical materials. One criterion that Cu$_2$CdSn$_4$ and α/β-Cu$_2$ZnSiS$_4$ met was phase matchability, where Cu$_2$CdSn$_4$ is phase matchable for $\lambda \geq 2100$ nm and α/β-Cu$_2$ZnSiS$_4$ is phase matchable for $\lambda \geq 1700$ nm.400 The phase matchability range for Cu$_2$CdSn$_4$ is larger than the commercially available AgGaSe$_2$ ($\lambda \geq 3100$), and α/β-Cu$_2$ZnSiS$_4$ has a larger range than the benchmark AgGaS$_2$ ($\lambda \geq 1800$).401 The melting points of Cu$_2$CdSn$_4$ and α/β-Cu$_2$ZnSiS$_4$ were found to be 930 °C and >1000 °C, respectively,400 which are within the same range as the currently used materials, ZnGeP$_2$ (1298 °C), AgGaSe$_2$ (998 °C), and AgGaS$_2$ (1002 °C).401 The area where Cu$_2$CdSn$_4$ and α/β-Cu$_2$ZnSiS$_4$ greatly outshine the commercially available materials is the optical transparency range, 1.2-25 μm and 0.7-25 μm, respectively.400 These values exceed ZnGeP$_2$ (0.74-12 μm), AgGaSe$_2$ (0.76-17 μm) and AgGaS$_2$ (0.48-11.4 μm).401 The second-order nonlinear optical susceptibility, $\chi^{(2)}$, of Cu$_2$CdSn$_4$ was found to be 65 pm/V, which is comparable to AgGaSe$_2$ that has a $\chi^{(2)}$ of 66 pm/V.400,401 While α/β-Cu$_2$ZnSiS$_4$ has a lower $\chi^{(2)}$ of 15 pm/V, the laser-damage threshold (LDT) was found to be 2.0 GW/cm$^2$ (1064 nm, 30 ps), one order of magnitude larger than Cu$_2$CdSn$_4$ (0.2 GW/cm$^2$ at 1300 nm, 30 ps) and AgGaSe$_2$ (0.2 GW/cm$^2$ at 1064 nm, 30 ps).401 Additionally, Cu$_2$CdSn$_4$ and α/β-Cu$_2$ZnSiS$_4$ exhibited third-order optical nonlinearity with a third-order susceptibility, $\chi^{(3)}$, of $(8.0\pm2.0) \times 10^4$ pm$^2$/V$^2$ and $(2.1\pm0.6) \times 10^4$ pm$^2$/V$^2$, respectively.400 These values are lower than the $\chi^{(3)}$ for AgGaSe$_2$ ($1.6 \times 10^5$
pm²/V²), but Cu₂CdSnS₄ is likely underestimated due to bandgap absorption. Thus, Cu₂CdSnS₄ and α/β-Cu₂ZnSiS₄ fit multiple criteria and are therefore potential candidates for IR NLO applications.

7.4 Major Findings of Chapter 6

Chapter 6 focused on the study of manganese substituted silver indium selenide, AgInSe₂:Mn. The compounds were found to be single-phase for Ag₁₋₂xMnxInSe₂ (x=0-0.07) and Ag₀.₉₅Mn₀.₀₅InSe₂. Using laboratory X-ray powder diffraction data, the structures of Ag₁₋₂xMnxInSe₂ (x=0-0.07) and Ag₀.₉₅Mn₀.₀₅InSe₂ were refined using Rietveld refinement and manganese was found to occupy the Ag (4a) site. The lattice parameters and unit cell volume were found to decrease with increasing manganese content and vacancies for Ag₁₋₂xMnxInSe₂ (x=0-0.07). Using XPS, the oxidation states were determined for each ion in Ag₁₋₂xMnxInSe₂. It was concluded that the addition of manganese did not alter the oxidation states of the other ions. For the Ag₁₋₂xMnxInSe₂ (x=0-0.07) series, the bandgap energy (~1.2 eV) was shown to increase with increasing manganese content. Careful analysis of the absorption edges of the series resulted in determining that the data could only be fit with a direct function, thus all compounds within the series were judged to have direct bandgaps, demonstrating that the substitution of manganese did not change the direct nature of the bandgap. Since compounds of the Ag₁₋₂xMnxInSe₂ (x=0-0.07) series, like the parent, are direct bandgap semiconductors, they are attractive candidates for solar cells due to the incorporation of lesser amounts of indium. The study provided a means to substitute AgInSe₂ with manganese allowing for physical property tuning in this system.
7.5 Broader Impacts

Several findings of this dissertation work are predicted to have an influence on future research in the area of DLSs. Six such outcomes have been selected for discussion below: 1) the importance of careful, whole pattern fitting of high resolution X-ray powder diffraction data, 2) the establishment of I$_2$-II-IV-VI$_4$ materials as a new class of IR NLO candidates, 3) the importance of broadband NLO studies, 4) the utility of XPS for determination oxidation states of ions in DLSs, 5) a general mechanism for doping AgInSe$_2$ and 6) the importance of studies coupling crystal structure, electronic structure and physicochemical properties.

In order to carry out physicochemical characterizations, first structural studies of the materials being investigated should be performed. As shown in Chapter 2, small differences within X-ray powder diffraction data can give rise to the discovery of a different structure. Thus, other materials that have had only the peaks indexed should be thoroughly investigated to determine if the small differences are unwanted second-phases or rather a new structure. While laboratory X-ray powder diffraction data can provide insight into phase identification, high-resolution synchrotron X-ray powder diffraction data is truly needed when verifying that only one polymorph exists within a powder, quantifying each phase within the sample, and determining site occupation factors. Accordingly, compounds with only lattice parameters and structure-type known, drive the need for high-quality and high-resolution X-ray diffraction data that can be carefully analyzed via Rietveld refinements.

The addition of Cu$_2$CdSnS$_4$ and α/β-Cu$_2$ZnSiS$_4$ as potential NLO materials has increased the awareness that quaternary DLSs are showing promise as IR NLO
materials.\textsuperscript{400} Hence, further analysis is necessary on related quaternary DLS systems. Furthermore, a firmer grasp of how bonding, bandgap, $\chi^{(2)}$, and LDT correlate is critical to access useful NLO materials.

Broadband studies of Cu$_2$CdSnS$_4$ and $\alpha/\beta$-Cu$_2$ZnSiS$_4$ found phase matchability of $\lambda \geq 2100$ nm and $\lambda \geq 1700$ nm, respectively. Here, we suggest that broadband studies should be carried out on previously reported materials, where phase matchability was only determined for one incident wavelength, 1.064 or 2.05 $\mu$m. For example, Sm$_4$GaSbS$_9$ and Gd$_4$GaSbS$_9$ were shown to have significant SHG responses and large optical transparency ranges, 1.75-25 and 0.75-25 $\mu$m; however, the materials were found to be non-phase matchable at 2.05 $\mu$m, yet they were only measured at that one incident wavelength.\textsuperscript{404} Additionally, compounds with the formulae AX$^{II}_4$X$^{III}_5$Se$_{12}$, where A= K, Rb, and Sc, X$^{II}$=Cd, and Mn, and X$^{III}$= Ga and In, exhibit large second order nonlinearity and possess wide optical transparency ranges, but have all been deemed non-phase matchable at 2.05 $\mu$m.\textsuperscript{405} These materials should be assessed at higher incident wavelengths. If phase matchable at longer incident $\lambda$, some of these materials may have a greater potential as candidates for NLO applications; however, an in-depth broadband study is essential in that determination.

XPS has been used in the determination of oxidation states as well as to investigate bonding interactions for Cu$_2$CdSiS$_4$, and $\alpha/\beta$-Cu$_2$ZnSiS$_4$.\textsuperscript{400} For these materials we find that the degree of ionic-covalency is important for the potential in NLO applications and we suggest that compounds with a higher degree of covalency should be targeted without decreasing the bandgap or changing states around the Fermi level. Therefore, measuring BEs of elements for the ions in other DLSs could provide insight in
how they might respond to NLO measurements. BEs were also measured for the constituent ions in AgInSe$_2$:Mn, where the oxidation state of manganese was found unchanging when a higher manganese content was used. Substitution of DLSs is an attractive route towards new solar cells and thermoelectric materials, due to the enhanced efficiencies. As substituting DLSs progresses into using elements with multiple possible oxidation states, the more XPS will be needed to confirm the oxidation states. Our work clearly demonstrates the utility of this method.

The substitution of manganese on the Ag(4a) site in the Ag$_{1-x}$Mn$_x$InSe$_2$ series may represent a general mechanism to substitute silver ions with higher valence dopants to be used in other related compounds. Additionally, using substitution in these types of materials has the potential to tune properties, like bandgap, that can eventually be used to target specific applications, such as in the area of thermoelectrics.

In conclusion, this work underscores the importance of in-depth studies of crystal structure, electronic structure, and physicochemical characterizations to reveal structure-property relationships. The influence that small, subtle structural changes can have on physicochemical properties of diamond-like semiconductors cannot be under-estimated. As more correlation between crystal structure, electronic structure, and physicochemical characterizations are determined, more predictive tools can be formulated and ultimately, materials can be selectively synthesized for specific applications. Furthermore, this work also paves the way for additional studies into structure-property correlations in DLSs. Some future avenues towards reaching this ultimate goal are outlined below.
7.6 Future Work

In the future, a synthetic procedure should be developed to prepare each polymorph of Cu$_2$ZnSiS$_4$ individually. Once separated, some of the physicochemical characterizations will need to be repeated. One important measurement to carry out is experimentally finding the bandgap energy of each polymorph, which has been found to correlate to some optical properties. Furthermore, optical property investigations of SHG, THG, and LDT should be repeated on the individual polymorphs. It is possible that one polymorph has a stronger nonlinear optical response than the other, thus making the original measurements of the mixture an underestimation of the properties.

A material with a higher degree of covalency generally leads to a larger $\chi^{(2)}$, whereas a wide bandgap commonly results in a better LDT. However, $\chi^{(2)}$ and LDT can both be large as shown in the case of Li$_2$CdGeS$_4$, demonstrating that $\chi^{(2)}$ and LDT are not mutually exclusive. Thus, a method is suggested to target materials with a higher degree of covalency without decreasing the bandgap as well as to not change the states around the Fermi level. The calculated electronic structures of all of the studied materials indicated that the top of the valence band is dominated by the hybridization of the Cu/Ag-$d$ and chalcogen-$p$ states. Near the top of the valence a minute contribution comes from the II or IV-metal, therefore other metals could be used with little change to the bandgap. Therefore, the quaternary DLSs with the formulae Cu$_2$CdSiS$_4$ and Cu$_2$ZnGeS$_4$ should be pursued. Density of states and Mulliken population analysis suggests that Cu$_2$CdSiS$_4$ could have a large LDT like that of $\alpha/\beta$-Cu$_2$ZnSiS$_4$; however, measurements would need to be conducted for verification. Additionally, due to Li$_2$CdGeS$_4$ showing a large SHG
response and large LDT materials with the formula Li$_2$-II-Si-S$_4$, where II= Zn and Cd should also be investigated for their potential as a NLO materials.

AgInSe$_2$ has recently been substituted with Zn on the Ag site and a ZT value of 1.05 ± 0.12 at 815 K was found, which is substantially larger than the undoped AgInSe$_2$ (ZT= 0.34 at 724 K). In this dissertation, it was found that adding an element with an oxidation of +2, a vacancy was also needed on the Ag site or unwanted secondary phases form. Thus, the formula Ag$_{1-2x}$-II$_x$-In-Se$_2$ could be used as a means to substitute elements with an oxidation state of +2, such as iron and chromium. Using this mechanism could result in the synthesis of multiple substituted AgInSe$_2$ materials, which could produce higher ZT values that would benefit future thermoelectric devices.

7.6 References


