Cu$_2$ZnSnSe$_4$: SYNTHESIS AND CHARACTERIZATION

by

Zhiqiang Wang

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Zhiqiang Wang

Approved: ______________________________________
S. Ismat Shah, Ph.D.
Professor in charge of thesis on behalf of the Advisory Committee

Approved: ______________________________________
Darrin Pochan, Ph.D.
Chair of the Department of Materials Science and Engineering

Approved: ______________________________________
Babatunde A. Ogunnaike, Ph.D.
Dean of the College of Engineering

Approved: ______________________________________
Ann L. Ardis, Ph.D.
Senior Vice Provost for Graduate and Professional Education
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Last but not least, my son is coming to the world in the May. I am so excited and want to say thank you to him. You will make me a better person and have always been my motivation to work harder.
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Thin film photovoltaic has attracted much attention for its high potential to decrease production cost to develop cost-effective and high performance solar cells. Among all these promising materials, chalcopyrite copper indium gallium selenide Cu(In, Ga)(S, Se)$_2$ have gained the highest reputation for its achieved high power conversion efficiency. Laboratory-scale conversion efficiency up to 20.3% has been recently achieved for a CIGS solar cell deposited on a glass substrate. Therefore, the successful commercialization of CIGS cell technology highly relies on the cost reduction. However, the element Indium in CIGS is not earth abundant and therefore hinders the further decrease in production cost. As a potential substitute, quaternary chalcogenide Cu$_2$ZnSnSe$_4$ (CZTSe) has received more attention nowadays, as it consists of all earth abundant elements and therefore is more environmentally friendly. So in this research, we focus on the synthesis and characterization of CZTSe.

In this research, quaternary Cu$_2$ZnSnSe$_4$ particles, useful for low cost solar cell synthesis, were successfully prepared using sonochemistry assisted solid state synthesis method. The pathways of the reactions during the synthesis as a function of the annealing temperature were studied by X-ray diffraction and energy dispersive X-ray spectroscopy (EDS) with the identification of the intermediate binary phases (Cu-Se, Zn-Se, Sn-Se), ternary phases (Cu-Sn-Se, Cu-Zn-Se) and the eventual formation of the quaternary phase Cu$_2$ZnSnSe$_4$. The obtained particles were characterized by X-ray diffraction (XRD) and UV-Vis optical absorption spectoscopy. The results showed that the annealing temperature of 450°C is optimal for the formation of pure
quaternary phase. However, the temperature range within which pure Cu$_2$ZnSnSe$_4$
could be obtained was very narrow and Cu$_2$ZnSnSe$_4$ decomposes to various binary and
ternary phases as the temperature is increased above the stability range. UV-Vis
absorption spectroscopy illustrated that the particles had high absorption of visible
light and had a direct band gap around 1.2 eV. These findings demonstrated a low-cost
and environmentally friendly method to synthesize CZTSe particles.
Chapter 1
INTRODUCTION

Energy is one of the most important issues we need to resolve to develop the economy and protect the environment. While most countries in the world have paid more attention to continuous development and environment protection, people nowadays realize the importance of the application of solar energy. Thin film solar cells, with the ability to minimize the manufacture costs for both raw materials and post-processing requirements, have attracted a lot attention. Now, amorphous Si, Cu(In, Ga)S₂ (CIGS) and CdTe have all been demonstrated to be good materials to make thin film solar cells. Among them, CIGS solar cells have the highest achieved efficiency, with the efficiency of small-area thin film cells being 20.3%. Although CIGS has good stability and radiation hardness, the high prices of elements such as indium and gallium may hinder cost-effective and large-scale production of CIGS based photovoltaic. [1] Therefore, Cu₂ZnSnSe₄ (CZTSe) quaternary compound is a very promising candidate for replacing CIGS. CZTS materials also have direct band gaps that range from 1 – 1.6 eV and a high absorption coefficient 10⁴ cm⁻¹ and are suitable for solar cell applications. [2-3]

The focus of this study is Cu₂ZnSnSe₄ (CZTSe). Since this material is tolerant to many types of defects, the techniques used for the synthesis of CZTSe have been numerous, including vacuum based [4-5] and solution based techniques in which either the material is created as a film directly or a powder is produced which then becomes the precursor of CZTSe ink. [6] It has been reported in the literature that the
formation of CZTSe is possible from the binary selenides of copper, zinc, and tin through solid-state reactions. [7] F. Hergert also reported that the formation of CZTSe is a concurrent process with two possible pathways:

\[
\begin{align*}
\text{Cu}_2\text{Se} + \text{ZnSe} + \text{SnSe} + \text{Se} &\rightarrow \text{CZTSe} \quad (1.a) \\
2\text{CuSe} + \text{ZnSe} + \text{SnSe}_2 - \text{Se} &\rightarrow \text{CZTSe} \quad (1.b) \\
\text{Cu}_2\text{Se} + \text{SnSe}_2 &\rightarrow \text{Cu}_2\text{SnSe}_3 \quad (2.a) \\
2\text{CuSe} + \text{SnSe} &\rightarrow \text{Cu}_2\text{SnSe}_3 \quad (2.b) \\
\text{Cu}_2\text{SnSe}_3 + \text{ZnSe} &\rightarrow \text{CZTSe} \quad (2.c)
\end{align*}
\]

Both these reactions schemes involve binary selenides that eventually lead to the formation of the quaternary compound, either as a direct reaction between the binaries or involving an intermediate ternary phase. Similar phase transformation reaction path is predicted by the effective heat of formation model which describes the probability of forming a certain compound based on the heat of formation of the compound.

The synthesis techniques previously utilized either involved high temperatures, vacuum evaporation or long reaction times. For example, solvothermal method can be conducted under a low temperature (~250°C) but it requires a long reaction time (~24 hr). [8-9] Standard solid state reaction usually requires a long time process of milling and the reaction temperature is also relatively higher (~500°C). [10-11] Co-evaporation that is used to form thin films is usually conducted under a temperature of ~450°C but it is a vacuum based process which affects the process cost and introduces scale-up issues. [12]
The research reported in this thesis is based on the EHF model based predictions of the reaction pathways of the synthesis of the CZTSe particles but instead of direct solid state reaction we applied sonochemistry assisted solid state method. Sonochemistry is the process of using ultrasound irradiation to induce rapid chemical reactions. Typically, ultrasound can create a temporary localized environment of high temperature of roughly 5000°C and high pressure of about 500 atmospheres. In addition, sonication also leads to high-velocity interparticle collisions and help accelerate the reaction. [13-15] We used stoichiometrically mixed elemental precursors for the synthesis of CZTSe. Just sonication of the mixture yielded a mixture of phases with very little to no sign of the desired quaternary phase and a post-sonication annealing was always required. The process parameters were optimized for the production of pure phase CZTSe which was characterized by various techniques to understand the structural transformations, chemistry, optoelectronic properties and the reaction pathways during the synthesis.
Chapter 2
EXPERIMENTAL METHODS

2.1 Sonochemistry

Sonochemistry is the application of powerful ultrasound to induce chemical reactions. Sonochemistry was developed during 1880s. It takes advantage of acoustic cavitation effect to create the necessary environment for the successful progress of chemical reaction. [16] When ultrasonic waves propagate in the liquid, it creates bubbles inside the liquid because of the intense vibration of liquid particle, which is induced by the ultrasonic waves. The creation, growth, and collapse of these bubbles will result in a temporary high temperature and high pressure environment. The temperature can go up to 5000 °C and the pressure can go up to 500 atmosphere, therefore it induces the reaction between reactants.

Sonochemistry has wide application in chemical reactions. The application of ultrasound can enhance the reaction rate and thus decrease the reaction time. It can also induce the occurrence of some reactions which cannot happen under normal situations. Because of all these advantages of sonochemistry, sonochemistry has received much attention and plays a significant role in the filed of synthetic chemistry. Sonochemistry have been applied to many fields of chemistry: organic synthetic chemistry, materials sciences, biological chemistry, analytical chemistry and polymer chemistry. [17-18]

In this research, we apply sonochemistry to induce the reaction between different elemental precursors: copper, zinc, tin, and selenium and study its effect on
the successful synthesis of CZTSe. The temperature obtained during the process of the collapse of bubbles is high enough to melt the metals. It also removes the oxides at the surface and thus lowers the surface activation energy to make the reaction easier to occur.
2.2 X-ray Diffraction (XRD)

X-Ray diffraction is a technique to analyze the crystal structure of materials through the diffraction effect of X-ray in the crystal. X-ray is a form of electromagnetic radiation with a wavelength ranging from 0.01 to 10 nanometers. Wilhelm Rontgen first discovered X-ray in 1895. X-ray is able to penetrate through specimens within a certain thickness. When the X-ray goes through the crystal, the X-ray interacts with the electrons in the crystal. The interaction between the X-ray and electrons in crystal can result in interference pattern of X-ray. There are constructive interference and destructive interference under different conditions. When the requirement for constructive interference is satisfied, the diffraction occurs. In 1913, Bragg put forward the famous Bragg’s law to explain the interference pattern:

\[ n\lambda = 2d\sin\theta \] (3)

where \( \lambda \) is the wavelength of the incident X-ray, \( d \) is the distance between two adjacent crystal planes, \( \theta \) is the incident angle, and \( n \) is the order of diffraction as shown in Figure 2-1. After that XRD has been widely applied to measure the average spacing between crystal planes, determine the orientation of a single crystal, determine the crystal structure of an unknown material and so on.
Figure 2-1 Bragg’s law

In this research, the XRD data are collected from Wide Angle X-ray Powder Diffraction instrument with Bragg-Brentano geometry. The X-ray source is Cu Kα1,2 radiation. The instrument works at 30 kV and 30 mA. Based on the collected XRD data, the Crystal structure and phase identification analyses of the samples were carried out by comparing with the Powder Diffraction Standards (JCPDS) database.
2.3 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is utilized to obtain high-resolution images of the samples and analysis of the surface of the samples. In SEM electrons are produced under high vacuum by two different ways: thermionic emission and field emission. These electrons usually have high energy ranging from 0.1 keV to 20 keV, and therefore electrons can interact with the atoms in the sample and most of them are scattered inelastically or elastically because of not having enough energy to penetrate the samples. There are various signals produced from scattering in bulk specimen: back scattered electron, secondary electron, auger electron, X-rays and so on. Figure 2-2 shows all these signals after the interaction between electrons and specimen. The SEM images are usually collected from secondary electrons through a secondary electron detector.

Figure 2-2 Electron/specimen interactions: primary and secondary signals
In our research, the morphology of our samples was investigated by using a field emission scanning electron microscope (JEOL JSM-7400F). The voltage of the electron source is 10 kV, and the penetration depth into the sample is around 1-1.5 µm.
2.4 Ultraviolet-Visible Spectroscopy (UV-Vis)

Ultraviolet-Visible spectrophotometry is a technique to study the optical properties of materials, for example thin films, particles, solutions and so on. The absorbance, transmittance, reflectance of samples can be collected in a preferred wavelength range. In this research, the absorbance of samples was collected through a Perkin-Elmer UV/Vis/NIR spectrophotometer in the wavelength range between 300 nm and 1200 nm. And Kubelka-Munk theory was applied to calculate the band gap of our samples.

According to semiconductor theory, band gap energy \( E_g \) can be calculated through the following equation:

\[
\alpha h\nu = A (h\nu - E_g)^n \quad (4)
\]

where \( \alpha \) is the absorption coefficient, \( A \) is a constant, and \( n \) equals to 1/2 for direct band gap. Therefore, the band gap could be obtained by the intercept of the linear part of the \((\alpha h\nu)^2\) versus \( h\nu \) plot.

In Kubelka-Munk theory, we can substitute \( \alpha \) with \( F(R_\infty) \) to estimate the band gap according to the following equation:

\[
F(R_\infty) = \frac{(1 - R_\infty)^2}{2 R_\infty} \quad (5)
\]

Where \( R_\infty \) is the diffuse reflectance. In our calculation, absorbance was used instead of \( R_\infty \). As it is difficult to get the absorption coefficient in this research, so we apply
the Kubelka-Munk theory and use $F(R_{\infty})$ as the estimated absorption coefficient to get our $(\alpha h\nu)^2$ vs. $E$ plot.
Chapter 3

EFFECTIVE HEAT OF FORMATION MODEL

3.1 Introduction

The change in the Gibbs free energy $\Delta G$ of a reaction process determines whether that reaction can happen or not. Therefore, Gibbs free energy has been applied to predict the process of reactions. However, for solid-state reactions the change of entropy is usually very small ($\sim 0.001 \text{ kJ deg}^{-1} \text{ mol}^{-1}$), which means the change of enthalpy $\Delta H$ can replace the change of Gibbs free energy $\Delta G$ as a good measure for predicting the reaction process of solid-state reactions. In 1992, R. Pretorius proposed an effective heat of formation model, which can be applied to predict compound phase formation sequence for binary reaction systems. [19] In this model, he found that the heat generated depends on both the available concentration of the limiting element and the concentration of limiting element in the compound to be formed. Based on this discovery, an effective heat of formation is defined as:

$$\Delta H' = \Delta H \times \frac{\text{Effective Concentration of Limiting Element}}{\text{Compound Concentration of Limiting Element}}$$ (6)
3.2 Phase Formation Sequence for Cu-Se System

For the Cu-Se system, there are three phases we take into consideration here, which are CuSe, CuSe$_2$ and Cu$_2$Se. According to the paper, the heats of formation values for them are -39.5 kJ/mol, -43.0 kJ/mol and -59.3 kJ/mol, respectively [20]. The above values were firstly transformed to values per atom before used to our calculation, which became -19.8 kJ/(mol·atm), -21.5 kJ/(mol·atm) and -29.7 kJ/(mol·atm) respectively. Figure 3-1 below shows the EHF plot for the Cu-Se system. According to the EHF model and the ratio of Cu and Se, we can see that CuSe will be formed first, since it has the lowest effective heat of formation value. The next phase to form depends on the element composition at the interface. If Se is abundant, the next phase to form will be CuSe$_2$ as it moves across the phase diagram to the right. If Cu is abundant, the next phase to form is Cu$_2$Se.

![Figure 3-1 EHF plot for Cu-Se binary system](image)

Figure 3-1 EHF plot for Cu-Se binary system
3.3 Phase Formation Sequence for Sn-Se System

For the Sn-Se system, there are only two possible phases known from the phase diagram, which are SnSe and SnSe$_2$. The heat of formation values for SnSe and SnSe$_2$ are -68.6 kJ/mol and -124.7 kJ/mol respectively [21]. The values per atom are -34.38 kJ/(mol·atm) and -41.68 kJ/(mol·atm) respectively. The EHF plot of the system is shown in Figure 3-2. According to the plot, SnSe$_2$ has the lower effective heat of formation, thus will be the first phase to be formed. The next phase to be formed is SnSe.

![Figure 3-2 EHF plot for Sn-Se binary system](image)

Figure 3-2 EHF plot for Sn-Se binary system
Chapter 4
SYNTHESIS AND CHARACTERIZATION OF QUATERNARY CZTSe

4.1 Crystal Structure of CZTSe

CZTSe belongs to the I₂-II-IV-VI₄ compound family. According to the literature, there are two primary crystal structures for I₂-II-IV-VI₄ compound family: the kesterite type structure and the stannite type structure. It turns out that CZTSe crystallizes into kesterite structure, which is verified by the neutron diffraction data of CZTSe samples. According to Cals Persson’s calculation, the kesterite structure is a more stable phase than stannite structure, therefore this can also be explained from the perspective of energy. [22] However, I will cover the introduction of both the kesterite type structure and stannite type structure here, because there are only small differences existing between them.
Figure 4-1 shows the two different types of structures. As we can see from the graph, the positions of anions are the same for both the kesterite structure and stannite structure. The only difference exists in the distribution of the cations. In the kesterite structure, the cation layers alternates with CuSn, CuZn, CuSn, CuZn layer by layer. However, in the stannite structure, the cation layers are alternating with ZnSn, Cu$_2$, ZnSn, Cu$_2$ layer by layer correspondingly. Also, because of the different distribution of Cu and Zn, we can notice that there are four different types of bonds for Se in the kesterite structure, while in the stannite structure there are only three.
### 4.2 Experimental Details

All sonication experiments were carried out on a Cole Palmer 500 W, 20 kHz ultrasonic homogenizer at a power output of 5-8 W. Elemental metal powders mixed with Se powders in near stoichiometric mole ratios, shown in Table 1, were made into suspension in a 5 ml vial by adding 1 ml of 2-cyanopyridine and the mixture was sonicated for 2 minutes. It has been reported that during sonication, organic liquids give out free radicals which can etch surfaces to remove the oxides from the particles. [23-24] Therefore, the surfaces have lower activation energies for reactions and in the presence of high speed interparticle collisions, rapid selenization takes place. As will be discussed later, the reaction pathways always go through binary (Cu-Se, Zn-Se, Sn-Se) and ternary phase (Cu-Sn-Se) before a stoichiometric quaternary compound is obtained. For this reason Cu concentration is kept lower than predicted by the formula to render more complete reactions. Se is kept above the stoichiometric composition to compensate for its loss at high temperatures since Se has a high vapor pressure at the post-sonication annealing temperatures. A combination of the Se loss and Cu deficiency gives the stoichiometric quaternary composition. All sonication experiments were done under flowing nitrogen to avoid any oxidation of the material as the suspension cooled down to room temperature.

After sonication, the suspensions were transferred to a 6.5 cm$^2$ glass substrates on which they were dried on a hot plate for 2 hours at 60°C. The temperature was kept low to prevent oxidation. Once dried, the samples were placed into the furnace and annealed at temperatures between 300 and 600°C in an Ar gas atmosphere. After annealing, the samples were allowed to cool down naturally under Ar gas atmosphere.
Crystal structure and phase identification analyses of the samples were carried out by X-ray diffraction (XRD) using a Rigaku D-max B diffractometer with Cu Kα₁ X-rays. The morphology was investigated by scanning electron microscopy (SEM) using a JEOL JSM-7400F microscope, which also had an Energy Dispersive Spectrometer for composition measurements. UV-Vis data were collected on a Perkin-Elmer UV/Vis/NIR spectrophotometer equipped with an integrating sphere over a wavelength range of 300-2500 nm.

4.3 Results and Discussion

4.3.1 Binary System

Figure 4-2a shows the XRD pattern of the Cu-Se as-sonicated sample. Cu and Se form α-CuSe, and some Se remains since the starting mixture was Se rich (1:2::Cu:Se). This result is consistent with the EHF model, which predicts that CuSe is the first phase to form. After annealing at 300°C, orthorhombic CuSe₂ compound forms and both CuSe₂ and CuSe coexist, shown in Figure 4-2b, as predicted by the phase diagram and the EHF model (Figure 3-1). As the temperature is increased to 400°C, the vapor pressure of Se becomes high and loss of Se from the mixture occurs. As a result, the XRD pattern from 400°C annealed sample shows mostly α-CuSe phase with weak peaks related to the new β-Cu₂Se phase. The 500°C annealed sample

<table>
<thead>
<tr>
<th>Molecular ratios for different reaction systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary system Cu:Se, Sn:Se, Zn:Se</td>
</tr>
<tr>
<td>Ternary system Cu:Zn:Se</td>
</tr>
<tr>
<td>Ternary system Cu:Sn:Se</td>
</tr>
<tr>
<td>Quaternary system Cu:Zn:Sn:Se</td>
</tr>
<tr>
<td>Quaternary system Cu:Zn:Sn:Se</td>
</tr>
</tbody>
</table>
XRD pattern (Figure 4-2d) shows peaks primarily from the cubic Cu$_2$Se phase and some remaining α-CuSe.

Sn-Se system shows no reaction in the as-sonicated sample or in the sample annealed at 300°C. The XRD patterns of these samples are shown in Figure 4-3a and 4-3b. These patterns clearly show peaks related only to elemental Sn and Se. The XRD pattern for the 400°C annealed sample shows peaks for SnSe$_2$ with small amounts of SnSe. SnSe$_2$ is predicted to be the first phase to form by EHF model followed by SnSe. As shown in Figure 4-3d, both of the two phases coexist up to about 628°C, which is the eutectic temperature of the binary Sn-Se system above which a liquid phase forms.

Similar to the Sn-Se binary system, we do not observe any reaction in the Zn-Se as-sonicated sample. Even after post-sonication annealing at 500°C, there is no reaction observed in the Zn-Se sample. This is probably due to the high eutectic temperature of 1360°C for the Zn-Se system. As shown in the XRD patterns in Figure 4-4, only peaks for elemental Zn and Se are observed in XRD patterns. Se peaks start to reduce in intensity and eventually completely disappear at 500°C and only Zn related peaks are observable. It is possible to form ZnSe binary phase from elemental Zn and Se powders but a sealed system is required to avoid Se loss. [25]
Figure 4-2 XRD patterns of Cu-Se binary samples: (a) as sonicated (b) annealed at 300°C (c) annealed at 400°C (d) annealed at 500°C
Figure 4-3 XRD pattern of Sn-Se binary samples: (a) as sonicated (b) annealed at 300°C (c) annealed at 400°C (d) annealed at 500°C
Figure 4-4 XRD pattern of Zn-Se binary samples: (a) as sonicated (b) annealed at 300°C (c) annealed at 400°C (d) annealed at 500°C
4.3.2 Ternary System

XRD results are shown in Figure 4-5 and Figure 4-6 for Cu-Sn-Se and Cu-Zn-Se systems, respectively. The XRD pattern for the Cu-Sn-Se (CTSe) as-sonicated sample shows only the reaction between Cu and Se (Figure 4-5a). After annealed at 300°C, the XRD pattern still shows no sign of reaction between Sn and Se. There are peaks for CuSe and CuSe$_2$, similar to the peaks observed in Cu-Se binary sample annealed at 300°C, except for additional peaks corresponding to elemental Sn. We can see that Se reacts with Cu first due to its affinity to chalcogens. [26] XRD pattern from sample annealed at 400°C starts to show peaks for the ternary phase Cu$_2$SnSe$_3$ with a small amount of residual cubic CuSe$_2$. At 500°C, we achieve single phase of Cu$_2$SnSe$_3$ which upon further annealing at 600°C shows grain refining indicated by the increase in peak intensities and decrease of the peak’s full width half maxima.

Similar to the CTSe system, only Cu-Se reaction is observed in the ternary Cu-Zn-Se (CZSe) as-sonicated samples (Figure 4-6a). In the 300°C annealed sample, XRD pattern shows peaks for CuSe$_2$, Zn and some residual Se. Just as in the binary system, as the temperature increases, CuSe$_2$ starts to dissociate and Cu$_2$Se becomes more stable. Therefore, for the 400°C and 500°C annealed sample, we find only the binary phase Cu$_2$Se along with ZnSe and elemental Zn. In the 600°C sample, ZnSe peak becomes stronger and sharper indicating more ZnSe formation and grain refinement.
Figure 4-5 XRD patterns of Cu-Sn-Se ternary samples: (a) as sonicated (b) annealed at 300°C (c) annealed at 400°C (d) annealed at 500°C (e) annealed at 600°C
Figure 4-6 XRD patterns of Cu-Zn-Se ternary samples: (a) as sonicated (b) annealed at 300°C (c) annealed at 400°C (d) annealed at 500°C (e) annealed at 600°C
Figure 4-7 SEM images of (a) Cu-Se sample annealed at 500°C (b) Zn-Se sample annealed at 500°C (c) Cu-Sn-Se sample annealed at 600°C (d) Cu-Zn-Se sample annealed at 600°C

Considering that we do not see any reaction between Zn and Se in the binary system whereas the Cu-Zn-Se ternary system show presence of ZnSe at high temperatures, we conclude that the formation of ZnSe phase in the Cu-Zn-Se system is attributed to the existence of Cu. Possibly Cu catalyzes the selenization reaction of Zn. This result can be explained by the metal reactivity theory. Zn is above Cu in the activity series of metals because it has lower electronegativity. At temperatures above 400°C, Cu has already been selenized and exists mainly in the form of Cu⁺ in Cu₂Se. Due to the lower electronegativity, it is easier for Zn to lose electrons to Se. Therefore, it can reduce the Cu⁺ ion in Cu₂Se and then bond with Se instead following the reaction:
Zn + 2Cu^{+} \rightarrow Zn^{2+} + 2Cu (7)

The enthalpy change of the reaction is -109 kJ/mol. [27] The negative value indicates that the reaction is exothermic and spontaneously going in the right direction. After being reduced, Cu continues to react with Se to form more Cu$_2$Se. The reaction is almost completed in the 600°C sample where most of Zn is reacted and transformed to ZnSe.

The SEM micrographs of the Cu-Se 500°C, Zn-Se 500°C, Cu-Sn-Se 600°C and Cu-Zn-Se 600°C samples are shown in Figure 4-7. Figure 4-7a of the binary Cu-Se sample displays the agglomerated cubic Cu$_2$Se crystals with relatively uniform surfaces. Figure 4-7b contains only the large Zn chunks with a diameters of ~6 µm with some residual Se. Most Se has evaporated. Figure 4-7c shows a relatively uniform ternary Cu$_2$SnSe$_3$. In the Figure 4-7d of Cu-Zn-Se ternary phase, we can see the hexagonal Zn particles in the center. The background contains mainly agglomerated cubic ZnSe and some fused orthorhombic Cu$_2$Se crystals in the lower left corner.

4.3.3 Quaternary System

4.3.3.1 XRD and SEM results

XRD patterns of quaternary samples, as-sonicated and annealed at different temperatures, are shown in Figure 4-8. The as-sonicated sample shows only peaks for CuSe in addition to the elemental Sn, Se and Zn peaks, in accordance with what was observed in the binary and the ternary systems. After annealing at 300°C, we see peaks for elemental Zn and Sn phases as well as for CuSe and CuSe$_2$ phases following the pattern that was observed in the CTSe sample annealed at the same temperature.
except for the additional Zn phase. We started to see the quaternary phase CZTSe peaks in the XRD pattern in the 400°C annealed sample. Ternary phase Cu$_2$SnSe$_3$ is also visible at 400°C, just as in the ternary samples. The quaternary phase forms rapidly from the reaction between Cu$_2$SnSe$_3$ and ZnSe due to the epitaxial relationship between these two phases, as described by F. Hergert and R. Hock. [7] However, the reaction does not complete. As a result, abundant ZnSe and Cu$_2$SnSe$_3$ phases are still present in the sample along with little amount of residual Zn. The reaction does come to a completion at 450°C and we obtain the pure quaternary phase. At 500°C the peaks for ZnSe become stronger, just as in the Cu-Zn-Se ternary phase, and the peaks for Cu$_2$Se become stronger as well. According to Redinger et al, once the quaternary phase is formed, it can decompose according to the following equilibrium equation:

$$\text{Cu}_2\text{ZnSnSe}_4 \leftrightarrow \text{Cu}_2\text{Se(s)} + \text{ZnSe (s)} + \text{SnSe (g)} + \text{Se (g)} \quad (8)$$

Therefore, we conclude that the reason peaks of ZnSe, Cu$_2$Se becomes stronger is because of the decomposition of the quaternary phase. To further confirm this, we annealed the sample at 600°C, we find that the peaks of Cu$_2$Se and ZnSe both become even stronger indicating that there is limit of temperature in the stability of CZTSe beyond which it starts to decompose. Another important thing to mention here is that the decomposition rate varies with different experimental conditions. In our experiment, Ar gas is kept flowing throughout the annealing and cooling process to prevent oxidation. The Ar gas may have slowed down the desorption of the SnSe phase and, as a consequence the decomposition rate of CZTSe also slows down. [29]
Figure 4-8 X-ray diffraction patterns of the quaternary samples (a) as sonicated, (b) annealed at 300°C, (c) annealed at 400°C, (d) annealed at 450°C, (e) annealed at 500°C and annealed at 600°C. The peak numbers indicated correspond to (1) Sn (2) Zn (3) Se (4) α-CuSe (5) CuSe₂ (6) β-Cu₂Se (7) ZnSe (8) CZTSe (9) α-Cu₂Se (10) Cu₂SnSe₃
The phase analysis results for the quaternary samples at different stages obtained from the XRD patterns in Figure 4-8 are summarized in Table 2.

Table 2: Phase analysis for quaternary samples at different stages

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Phase Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>As sonicated</td>
<td>α-CuSe, Sn, Se, Zn</td>
</tr>
<tr>
<td>300°C</td>
<td>Zn, Sn, α-CuSe, CuSe₂</td>
</tr>
<tr>
<td>400°C</td>
<td>Zn, CZTSe, Cu₂SnSe₃, ZnSe, β-Cu₂Se</td>
</tr>
<tr>
<td>450°C</td>
<td>CZTSe</td>
</tr>
<tr>
<td>500°C</td>
<td>α-Cu₂Se, β-Cu₂Se, CZTSe, Cu₂SnSe₃, ZnSe</td>
</tr>
<tr>
<td>600°C</td>
<td>α-Cu₂Se, β-Cu₂Se, CZTSe, Cu₂SnSe₃, ZnSe</td>
</tr>
</tbody>
</table>

The morphological evolution of the sonication and annealing process is studied with SEM. Figure 4-9 shows the SEM micrographs of the quaternary as-sonicated and annealed samples at different temperatures. Figure 4-9a shows the SEM micrograph of the as-sonicated samples and as the X-ray diffraction showed, the only reacted phase present is CuSe along with all the other unreacted elements. The 300°C sample shows mainly the sintered grains of the orthorhombic CuSe₂ phase with small amounts of CuSe and some unreacted elements. CZTSe phase starts to form between 300°C and 400°C. Figure 4-9c displays the SEM micrograph of 400°C annealed sample with agglomerated small particles composed of the quaternary, ternary and binary compounds. At 450°C, the sample is pure CZTSe and the micrograph shows a non-uniform distribution of CZTSe crystals. As the annealing temperature increases, the CZTSe phase starts to decompose. In Figure 4-9e we can see the triangular shaped Cu₄Se crystal grains with {111} facets, confirmed by EDX and XRD. The other phase present include ortho-Cu₂Se, CZTSe, Cu₂SnSe₃, and ZnSe. At 600°C, Figure 4-9e, the
decomposition continues with the formation of ortho-Cu$_2$Se, cub- Cu$_2$Se, CZTSe, Cu$_2$SnSe$_3$, ZnSe phases.

Figure 4-9 SEM micrographs of CZTSe sample: (a) as sonicated (b) annealed at 300°C (c) annealed at 400°C (d) annealed at 450°C (e) annealed at 500°C (f) annealed at 600°C
4.3.3.2 UV-Vis Spectroscopy

The optical parameters were measured for the quaternary sample annealed at 450°C over a wavelength range of 300-2500 nm. The results are plotted in Figure 4-10 showing the absorbance curve vs. wavelength in the visible range with an inset plot of $(\alpha h\nu)^2$ as a function of photon energy. The discontinuity in the absorbance curve is due to the change of lamp in the device at the wavelength of around 850 nm. The band gap energy obtained from this graph is 1.2 eV, which is in good agreement with the reported values in the literature indicating the existence of the quaternary compound confirming the pure quaternary phase. [15, 28, 29]
Figure 4-10 UV-Vis absorbance spectrum for the pure CZTSe quaternary phase. The discontinuity in the absorbance curve is due to the change of lamp in the device at the wavelength of around 850 nm.
Chapter 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions
In this research, a sonochemical method is used to help the formation of the Cu$_2$ZnSeSe$_4$. The phase transformation reaction path during the annealing of the as-sonicated sample was also investigated. The phase analyses of powders show that only a reaction between Cu and Se elemental precursors was observed after sonication with other elements not participating in the reaction. Post-sonication annealing is required for further reactions. CZTSe starts to form in samples annealed at 400 °C and above. There is a small window of temperature, around 450 °C, within which a pure CZTSe phase could be obtained. As the temperature is increased above this range, the quaternary phase starts to decompose. The band gap of the pure quaternary phase was measured from the UV-Vis data and it is 1.2 eV, which matches well with the reported values for the CZTSe materials.

5.2 Recommendations
In this research, the pure quaternary phase CZTSe was successfully synthesized through the two-step sonication and annealing process. However, the size of the particles, as we can see from the SEM images, is not uniform. Therefore, we can further tune our process to get better results. There are several things we can try to achieve that: (a) different solvent (b) different sonication time. Solvent is very important in the sonication process so we can try other possible solvent to see if it helps decrease the particle size and make particles uniform. Sonication time is another
parameter we can adjust easily during the process and obviously the particle size is affected by the sonication time.

As CZTSe is a promising photovoltaic material, it should always be used to make a solar cell and test the efficiency. While in this research we don’t do so, therefore we can make a device based on the material we have synthesized and run a test for all the useful parameters for the device.
REFERENCES


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