

DISSERTATION

HOT INJECTION SYNTHESIS AND CHARACTERIZATION OF COPPER ANTIMONY
SELENIDE NON-CANONICAL NANOMATERIALS TOWARD EARTH-ABUNDANT
RENEWABLE ENERGY CONVERSION

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ABSTRACT

HOT INJECTION SYNTHESIS AND CHARACTERIZATION OF COPPER ANTIMONY SELENIDE NON-CANONICAL NANOMATERIALS TOWARD EARTH-ABUNDANT RENEWABLE ENERGY CONVERSION

Renewable and carbon-free energy generation has become a critically important field as the global population continues to increase. Further, the ample supply afforded by natural resources such as sunlight and geothermal heat are attractive options that can be harnessed using technologies like photovoltaics and thermoelectrics. There is a growing interest in searching for novel materials that exhibit high efficiencies in these devices, ideally composed of earth abundant, non-toxic materials. This search is aided by theory, which has identified several families of compounds with interesting structure types that may exhibit properties amenable to incorporation in high efficiency devices. However, many of these materials have not yet been thoroughly evaluated for photovoltaics or thermoelectrics. This dissertation is focused on developing the synthesis and describing the basic characterization of nanoparticles of members of the compounds in the Cu-Sb-Se series, of which syntheses have been developed for Cu_3SbSe_4 and Cu_3SbSe_3 and are described in this dissertation.

Herein, we describe a hot-injection route for the formation of Cu_3SbSe_4 and Cu_3SbSe_3 nanocrystals. In order to place this work in context, the first chapter of this dissertation provides a detailed summary of the literature investigating the Cu-Sb-Se family of compounds. Here, the highest thermoelectric efficiencies have been achieved for Cu_3SbSe_4 while Cu_3SbSe_3 is not yet comparable thermoelectrically to Cu_3SbSe_4 nor as efficient as the photovoltaic material CuSbSe_2 .

The second chapter details the development of a hot injection synthesis of Cu_3SbSe_4 nanocrystals. In order for these materials to be applied as electronic materials in real devices, their stability and function under ambient conditions is of interest. Therefore, we studied the changes in electronic conductivity as a function of exposure to atmosphere. The conductivity increase was attributed to a hole mobility increase, and this was further correlated to structural oxidations.

Chapter 3 details development of a synthesis for phase-pure Cu_3SbSe_3 nanodiscs. This material has become of interest recently for photovoltaic applications due to its acceptable band gap for solar absorption. While the synthesis of nanoscale Cu_3SbSe_3 has been reported, these results have not been reproduced, and property measurements among these limited works vary. Therefore, a robust synthesis was developed and initial optical and photoelectrochemical properties were measured and are reported in this dissertation that demonstrate photoactivity in thin films of the Cu_3SbSe_3 nanodiscs.

In the fourth chapter, a more vigorous exploration of the nanodisc morphology observed in Cu_3SbSe_3 is reported. As a degree of self-assembly is observed in stacks of the nanodiscs, the morphology is investigated to understand how tuning nanocrystal morphology, size, and surface might affect the resulting particle interactions. To this end, a double injection synthesis was developed wherein the products exhibit optoelectronic properties similar to those of the original single injection reaction.

Chapter 5 entails the electrochemical investigation of the copper antimony selenide nanostructures. Electrochemical measurements to experimentally elucidate the electronic structure are reported, and a photovoltaic architecture is proposed for a Cu_3SbSe_3 -absorber layer device. Further, the presence of a thiol has been demonstrated to be critical to not only morphology within the Cu_3SbSe_3 synthesis but also the product phase formation. Therefore, initial

measurements and challenges with *in-situ* electrochemical exploration of precursor reactivity are reported.

Finally, chapter 6 briefly emphasizes the major findings within this dissertation. The experimental results for both Cu_3SbSe_4 and Cu_3SbSe_3 syntheses are reiterated. Further, additional directions for future work with this system are suggested. These primarily focus on fabrication of a Cu_3SbSe_3 photovoltaic cell to begin understanding photogenerated carrier transport. This can be extended through applying knowledge gained by understanding disc stacking to improve film deposition and electronic properties within Cu_3SbSe_3 materials. Finally, development of an electrochemical measurement system for use in oleylamine media would allow a new perspective on investigation of colloidal nanocrystalline formation. These proposed experiments would contribute to their respective fields in the broader context of expanding search criteria for novel photovoltaic materials, addressing the challenge of grain boundary recombination sites in photovoltaic nanocrystals, and providing tools for exploring nanoparticle synthesis.

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CHAPTER 1

COPPER ANTIMONY SELENIDES: MATERIALS FOR EARTH ABUNDANT ENERGY CONVERSION[†]

1.1 Need for Energy Generation

As the human population expands, there is a proportional growth in the demand for more energy generation. Currently, we utilize a wide variety of energy sources, including nuclear, fossil fuels, and renewables among others. It is this last class that will be of interest looking to the future due to its potential to generate large quantities of energy safely and, depending on the materials used and their manufacturing methods, without consuming limited resources.

Renewable energy is a burgeoning field, consisting of energy generation and conversion sources such as thermoelectric, photovoltaic, hydroelectric, wind, and biomass. For the purposes of this review, we will not focus on combustion of biomass due to its negative impact on the environment. Likewise, wind and hydroelectricity are primarily mechanical sources of energy, and is therefore outside the scope of this review. We will instead focus on photovoltaic (PV) and thermoelectric (TE) sources.

[†] This dissertation chapter has been prepared and formatted for submission to *Sustainable Energy & Fuels*. It provides an introduction to the need for novel earth-abundant energy generation and conversion materials. Later, a thorough review of the literature surrounding CuSbSe₂, Cu₃SbSe₃, and Cu₃SbSe₄ is detailed focusing on their application to photovoltaic and thermoelectric energy generation. Finally, a brief statement on the challenges presented by selenium in colloidal nanocrystalline synthesis is made.

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Design principles for these materials should focus on maximizing efficiency. This means that for PV, they must absorb solar radiation with large absorption coefficients and direct band gaps in the appropriate range and possess adequate carrier transport properties to minimize recombination losses. For TE, they should possess a large value of ZT (>1) at their temperature of maximum performance. Further, given that one of the major impediments to implementation of renewable energy generation sources on a larger scale is the substantial cost of initial module fabrication/setup, energy generation materials should be composed of earth-abundant elements that can be extracted with minimal cost, in order to minimize the cost of material extraction. As a final selection criterion, the constituent elements present in these materials should not be toxic to either humans or the environment. Even though the materials should not leech into their surroundings during normal device operation, an ideal material would be safe in case of accidents or disposal. While current materials for PV and TE often involve rare or toxic elements such as Cd, In, and Te, the Cu-Sb-Se system (CuSbSe_2 , Cu_3SbSe_3 , and Cu_3SbSe_4) have been preliminarily explored as earth-abundant and less toxic alternatives. This review will first briefly describe how PV and TE devices work, and areas of focus for increasing efficiency in each case. Then we will comprehensively detail the work that has been reported for these systems, while suggesting some directions in which we recommend these materials should be further investigated.

1.2 Thermoelectrics Overview

Thermoelectric modules find application in many settings such as automotive heaters,¹ industrial waste heat scavenging,² cooling,³ and a variety of other applications in

which reliability and a lack of moving parts are advantageous.⁴ One of the major benefits to thermoelectrics is their ability to function without any moving parts. These materials utilize the thermoelectric effect (a combination of the Seebeck, Peltier, and Thomson effects) which describe the transport of electricity and heat. Here, a thermal gradient causes diffusion of electronic carriers within the material which generates a potential difference. This process can be exploited for thermoelectric energy generation. The opposite effect can also be used in which an electric potential is applied to a thermoelectric material for Peltier cooling or heating.

Thermoelectric devices are governed by the general equation:

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

where ZT is the thermoelectric figure of merit, S is the Seebeck coefficient, σ is the electronic conductivity, and κ is the thermal conductivity. For commercial applications, a $ZT \geq 2$ has been suggested to be feasible, though most cutting-edge thermoelectric materials only exhibit a ZT slightly greater than 1. The dominant TE materials are governed by their specific application, as the thermoelectric figure of merit has a temperature dependence.

Through the equation for the thermoelectric figure of merit, it's clear that a high electronic conductivity is desirable, while minimizing thermal conductivity is equally important. The separation of these two phenomena is the key challenge in the field of thermoelectrics. An ideal material would have the characteristics of a “phonon glass electron crystal” (PGEC)⁵ for this exact reason, as an electron crystal should exhibit good carrier transport properties, while a phonon glass should serve to efficiently scatter phonons thereby decreasing the thermal conductivity as phonons are a major contributor to heat transport in solid materials. There have been many attempts to obtain materials where this

is the case, and a wide variety of materials have been studied to this end.⁶ Further, there are many different approaches to obtain a PGEC.

One example of a class of thermoelectric compounds is skutterudites.^{7,8} These materials are of the CoAs_3 structure type, resembling a significantly distorted perovskite. At the center of this structure is a void that can be filled with a large metal atom. The void filling atom acts as a strong phonon scattering center, leading to desirably low thermal conductivities in this type of material, while the atoms that provide the framework for the structure are responsible for the electronic conductivity of the compound. Further, the species of filling atom can be tuned for improved electronic properties such as dopant concentration. Similar to skutterudites, clathrates are a common type of open-framework solid material that can accommodate large electropositive atoms.⁹ The “rattling” ability of the guest atoms in these skutterudites and clathrates has been proposed as a method of lowering thermal conductivity, and thereby increasing overall ZT of these materials.

Another method of increasing phonon scattering (and by extension decreasing thermal conductivity) is utilization of a disordered structure type. One such material, $\beta\text{-Zn}_4\text{Sb}_3$, is a moderate temperature p-type material, with ZT as high as 1.3 at 670 K.¹⁰ This material embodies the phonon-glass electron-crystal concept well.^{11,12} However, its use is limited as it decomposes to form ZnSb and Zn at its melting temperature of 841 K.

Despite not having rattling atoms or a disordered structure, PbTe is another example of a viable midrange temperature thermoelectric material. Crystallizing in the simple NaCl structure, the lattice thermal conductivity of PbTe has an inversely proportional dependence on temperature. Further, PbTe can be doped either p-type or n-type.

Layered materials represent another structure type that has demonstrated potential for high ZT thermoelectrics. The flagship material in this class is Bi_2Te_3 . Layers of Bi_2Te_3 are composed of five atomic layers stacked along the c-axis of the unit cell. Like PbTe , this material has been doped both p-type (by alloying with Sb) and n-type (by alloying with Se). For superlattices of layered materials like this, a ZT up to 2.4 has been achieved.¹³ This comes from a lattice thermal conductivity an order of magnitude lower than many other high-ZT TE materials, coupled with electron mobility between layers as high as mobility within layers.

Also within the realm of anisotropic TE materials is SnSe , which has shown the highest ZT of any bulk as-grown material to date. A layered structure like Bi_2Te_3 , SnSe has exhibited a ZT up 2.6 within the plane of the layers,¹⁴ demonstrating that its in-layer TE properties can be highly desirable.¹⁵

These are a sampling of materials aimed to demonstrate the wide variety of structure types employed to maximize ZT. The examples highlighted above are primarily binary compounds, and are composed of heavy elements. The exploration of more complex ternary compounds may open up new directions for decoupling electrical and thermal conductivity toward the goal of higher ZT. There are many other materials not covered here that are applied toward TE generation or heating/cooling. It's also important to note that while we have detailed various structure types, there are other strategies to improve thermoelectric function. These subjects are thoroughly detailed elsewhere,^{6,16-18} and so we will focus on the use of composition and crystallite structure to improve electronic and thermal transport in a series of earth-abundant materials.

1.3 Photovoltaics Overview

The sun provides more energy incident on Earth in just one hour than humans currently use in a full year. Therefore, a cheap, convenient method of converting this light and heat would be ideal as a clean source of energy. In order to generate electrical power from incident solar radiation, a PV device needs to demonstrate good optical absorption as well as good charge transport properties. Photovoltaic operation is governed by the equation for power conversion efficiency:

$$\eta = \frac{J_{sc}V_{oc}FF}{P_{in}}$$

where η is the power conversion efficiency, J_{sc} is the short circuit current density, V_{oc} is the open circuit potential, FF is the fill factor, and P_{in} is the incident power of radiation. High efficiency devices must exhibit strong optical absorption properties to generate a large number of excitons, but also demonstrate the ability to efficiently transport these materials throughout a device.

Here we begin the discussion of modern photovoltaic technologies with a brief description of the three generations of PV materials. Generation I is crystalline silicon modules. Silicon is an intrinsic semiconductor, able to be doped either p-type or n-type. This makes it desirable for homojunction cells. Further, silicon is extremely abundant on Earth which makes it an attractive component for solar cells (although the processing for purifying silicon from silicon dioxide is a fairly expensive process). However, crystalline silicon has a few major drawbacks and challenges such as its indirect band gap and poor optical absorption, which have been detailed elsewhere.¹⁹⁻²¹

To combat these shortcomings, generation II materials were investigated which involve thin-film PV materials. To minimize the need for a large amount of sample,

materials possessing a high optical absorption coefficient and ideal direct band gap of 1.34 eV (according to the Shockley-Queisser limit)²² were explored. Among the most highly employed materials in the generation II category are CdTe, and Cu(In,Ga)Se₂ (CIGS). These have recorded high efficiencies with CdTe reaching 22.1%²³ and CIGS reaching 22.6%.²⁴ However, these materials utilize cadmium which is undesirable due to its toxicity, and indium or tellurium, which are rare elements and may increase the cost of module production.

Generation III materials are currently pushing the boundary of PV technology in multiple directions. This broad category encompasses nanomaterials, polymer cells and organic photovoltaics, hybrid organic-inorganic perovskites, and multi-junction cells. These materials are being investigated for a variety of reasons such as lowering cost of components and processing as well as increasing efficiency. The cutting-edge materials here are too numerous to describe in this context, but it will suffice to say that the commercial potential for this generation is still too low to pursue for now, though they have the potential for a lower cost-per-watt than even generation II offers.

Considering the aforementioned ideal properties for energy generation materials, a large body of work has investigated earth-abundant PV alternatives. This may aid in commercialization of these technologies as earth-abundant material extraction costs may be lower than those of current generation II materials leading to better cost per watt generated.²⁵ Work in this field has been spearheaded by a focus on Cu₂ZnSnS₄ (CZTS), Cu₂ZnSnSe₄ (CZTSe), and the mixed chalcogenides (CZTS_xSe_{1-x}). These compounds are composed of all earth-abundant elements, and possess compositionally tunable direct bandgaps of 1.1-1.5 eV.²⁶⁻²⁹ A maximum certified power conversion efficiency of 12.6%

has been reported in this material,³⁰ but in general devices suffer from a limited open circuit potential, which has been hypothesized to be due to a large degree of cation disorder.^{31,32}

Despite the substantial progress with current PV technologies, there are still no high efficiency (>13%), earth-abundant materials that have been successfully commercialized. With this in mind, there have been several computational works that use search criteria such as band gap, earth abundance, and optical absorption to propose novel materials of interest.³³ Yu et al. have analyzed electronic properties of materials using density functional theory and suggest that there are two electronic structures that are worthy of investigation for PV: semiconductors where the smallest band gap is direct in nature, and those where the smallest gap is indirect, but there is a direct gap close in energy above the smallest transition.³⁴ They expanded upon this work to calculate the theoretical photovoltaic efficiencies of 300 different Cu-M-Ch (M = P, As, Sb, Bi; Ch = S, Se) compounds according to their spectroscopic limited maximum efficiency (SLME) metric that accounts for the type of band gap transition, the magnitude of the band gap, and the optical absorption profile all using the HSE06 hybrid functional.³⁵ Similarly, Zhang et al. undertook a similar study, though they employed a modified Becke-Johnson potential (mBJ).³⁶ These works have proposed several key materials worthy of investigation that may achieve high power conversion efficiencies while being composed of only earth-abundant constituent elements.

While theoretical works like these have paved the way for investigation of many new earth-abundant systems, to date none of these has surpassed the power conversion efficiency achievable with CZTSSe. However, several new interesting materials have been realized. These include ZnSnP_2 , SnS , $\text{Sb}_2(\text{S,Se})_3$, $\text{Cu}_2(\text{Sn,Ge})\text{S}_3$, FeS_2 , and copper

antimony chalcogenides among others. Progress with these materials can be viewed in Figure 1.1.

Of these materials, copper antimony chalcogenides possess a variety of interesting aspects, such as the presence of lone pairs, interesting structures (deviations from the typical diamondlike lattice including lower symmetry and layered structures), and strong optical absorption. Progress for CuSbS_2 has been reviewed by Krishnan et al.³⁷ and Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ have also demonstrated potential for applications in photovoltaics.³⁸⁻⁴² Despite the more complete body of work for copper antimony sulfides, copper antimony selenides may exhibit more desirable electronic properties and stronger optical absorption.⁴³

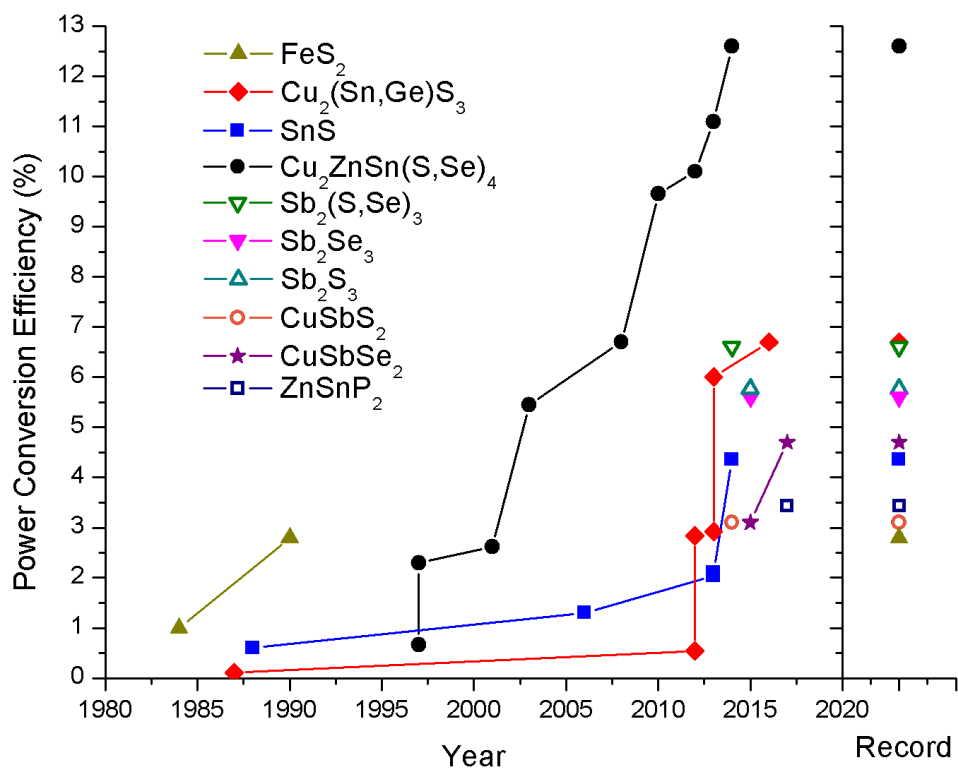


Figure 1.1 Power conversion efficiencies of a variety of earth-abundant absorber materials. The “Record” column compares the maximum achieved efficiency of each material.

1.4 Cu-Sb-Ch Structures

As we have previously mentioned, energy conversion and generation methods from earth-abundant materials are of critical and increasing importance. Common PV and TE materials are often expensive, with costs driven up due to the scarcity of their constituent elements. This has brought about a search for materials that are safe, cheap, and abundant. One such family of compounds is the copper antimony selenides. These include CuSbSe_2 , Cu_3SbSe_3 , and Cu_3SbSe_4 . The structures of these can be seen in figure 1.2. These features have been exploited for a variety of reasons, as will be detailed later in this review.

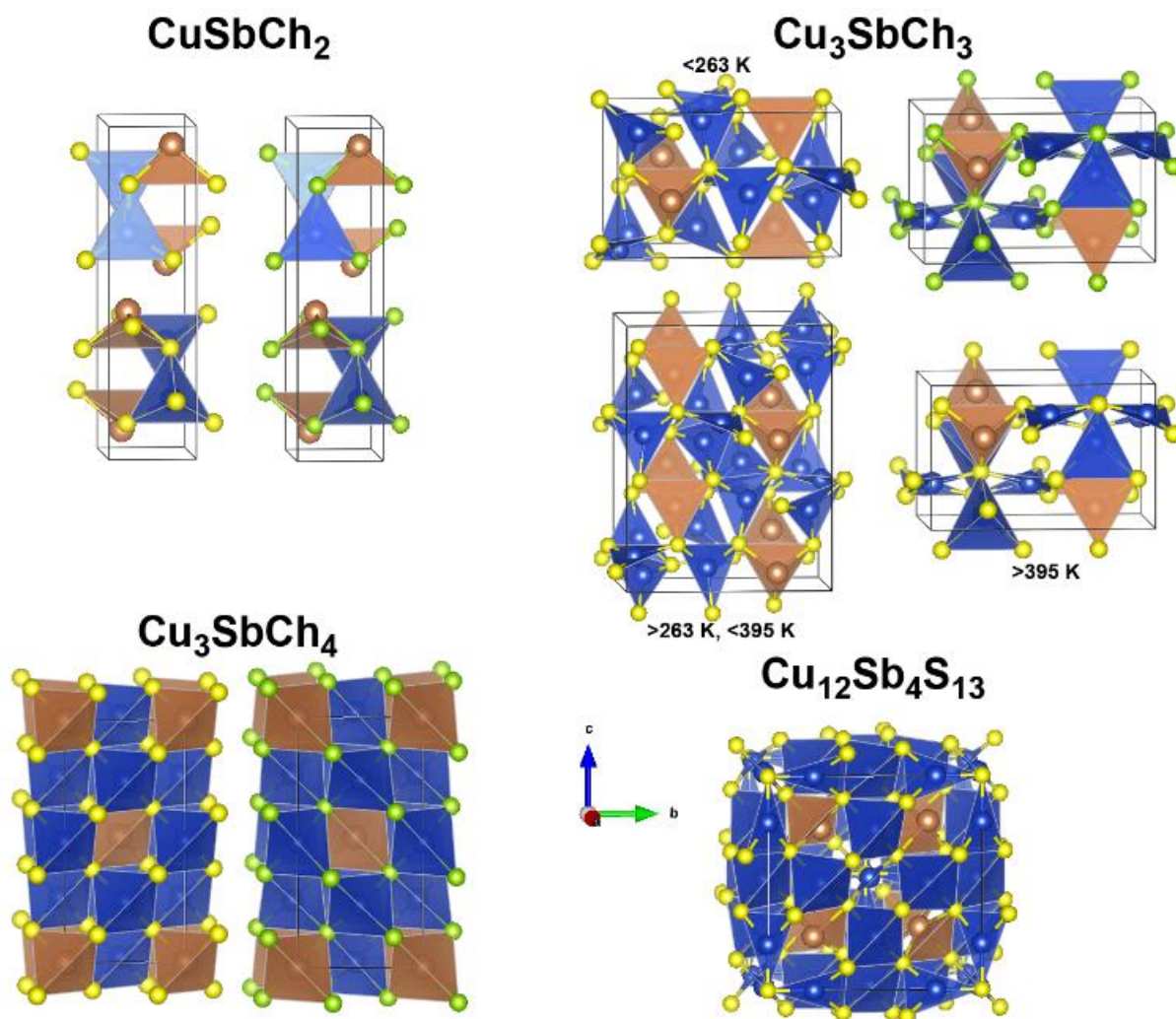


Figure 1.2 Crystal structures of the Cu-Sb-Ch phases. Blue is copper, brown is antimony, yellow is sulfur and green is selenium. CuSbCh_2 and Cu_3SbCh_4 are isostructural between sulfur and selenium analogues. Cu_3SbS_3 exhibits polymorphism while Cu_3SbSe_3 does not, and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ has no analogous selenium stoichiometry.

The antimony-rich endmember of these materials, CuSbSe_2 , crystallizes in the orthorhombic $Pnma$ space group (SG #62).⁴⁴⁻⁴⁶ This diselenide phase forms a layered structure, with two unique Se positions. It has layers four atoms thick and two layers per unit cell. The structure can be summarized by detailing the corner-sharing CuSe_4 tetrahedra and SbSe_3 trigonal pyramids, with the lone pair of the Sb^{3+} extending into the interlayer gap. Interestingly, it should be noted that CuSbSe_2 crystallizes in the wurtzite-based chalcostibite structure, as opposed to the chalcopyrite structure obtained for other I-III-VI₂ materials like CIGS.^{47,48}

The highest symmetry member of this family (as observed through their corresponding simulated X-ray diffraction patterns, figure 1.3) is the tetraselenide Cu_3SbSe_4 . This structure crystallizes in the tetragonal $I-42m$ space group (SG #121) and is characterized by corner-sharing tetrahedra of CuSe_4 and SbSe_4 .⁴⁹ There are four unique

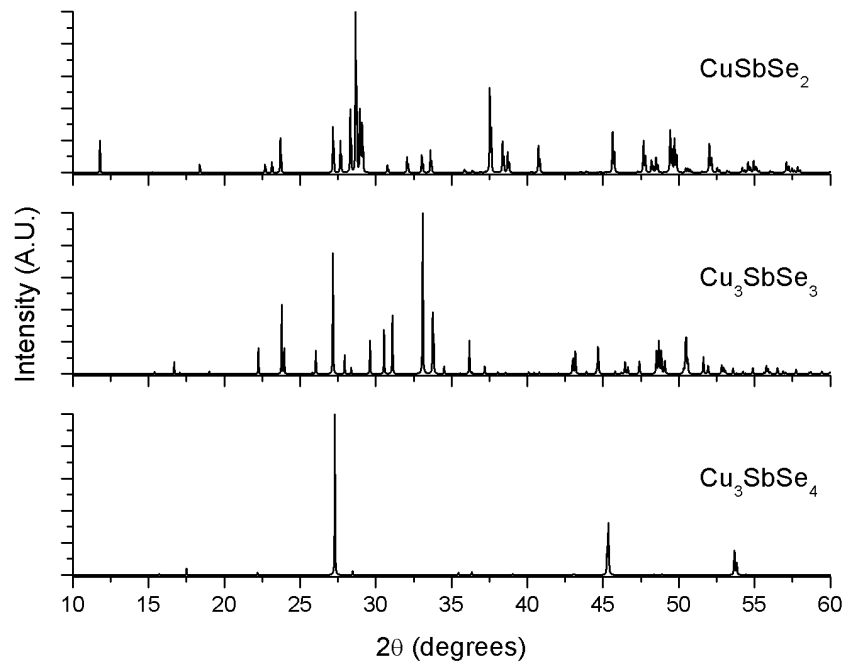


Figure 1.3 Simulated X-ray diffraction patterns of Cu-Sb-Se phases.

unit cell constituents, with the two copper positions differing by position along the *c*-axis (either in the plane of Sb or not).⁴⁹ This phase is also known as the mineral permingeatite, and is the only one among the Cu-Sb-Se materials so far discovered in nature.

In contrast, the triselenide phase exhibits the lowest symmetry of the Cu-Sb-Se materials as well as claims the title for being the most copper-rich phase. This material is found in the orthorhombic *Pnma* phase, which can be broken down into five irreducible positions with one Sb, two Cu, and two Se sites in the unit cell.⁵⁰ There are planes of tilted corner-sharing CuSe₃ trigonal polyhedra perpendicular to the *c*-direction. Between these are SbSe₃ trigonal pyramids and CuSe₄ tetrahedra that share a common edge but connect to the network of CuSe₃ trigonal polyhedra at corners.

It is also necessary to place the crystallography of Cu-Sb-Se materials into context. Of the copper antimony chalcogenides, both sulfides and tellurides exist apart from the selenide phases. As these materials are most often studied for tellurium-free alternatives, the copper antimony tellurides are not well studied, though CuSbTe₂ and Cu₃SbTe₄ have both been experimentally synthesized, and some preliminary properties have been investigated.^{51,52} To the contrary, the sulfides are the most well-studied compounds in this system (Figure 1.4).

Unlike the copper selenoantimonates, there are four known copper antimony sulfide phases. These consist of CuSbS₂, Cu₃SbS₃, Cu₃SbS₄, and Cu₁₂Sb₄S₁₃. Interestingly, the chalcostibite (CuSbS₂) and famatinite (Cu₃SbS₄) crystals are isostructural with their selenium analogues.^{44,49,53,54} However, Cu₃SbS₃ exhibits polymorphism with the material crystallizing in the orthorhombic *P2₁2₁2₁* phase (SG #19) below 265 K.⁵⁵ From 263-395 K, it forms the monoclinic *P2₁/c* (SG #14).⁵⁶ Finally, for temperatures greater than 395K

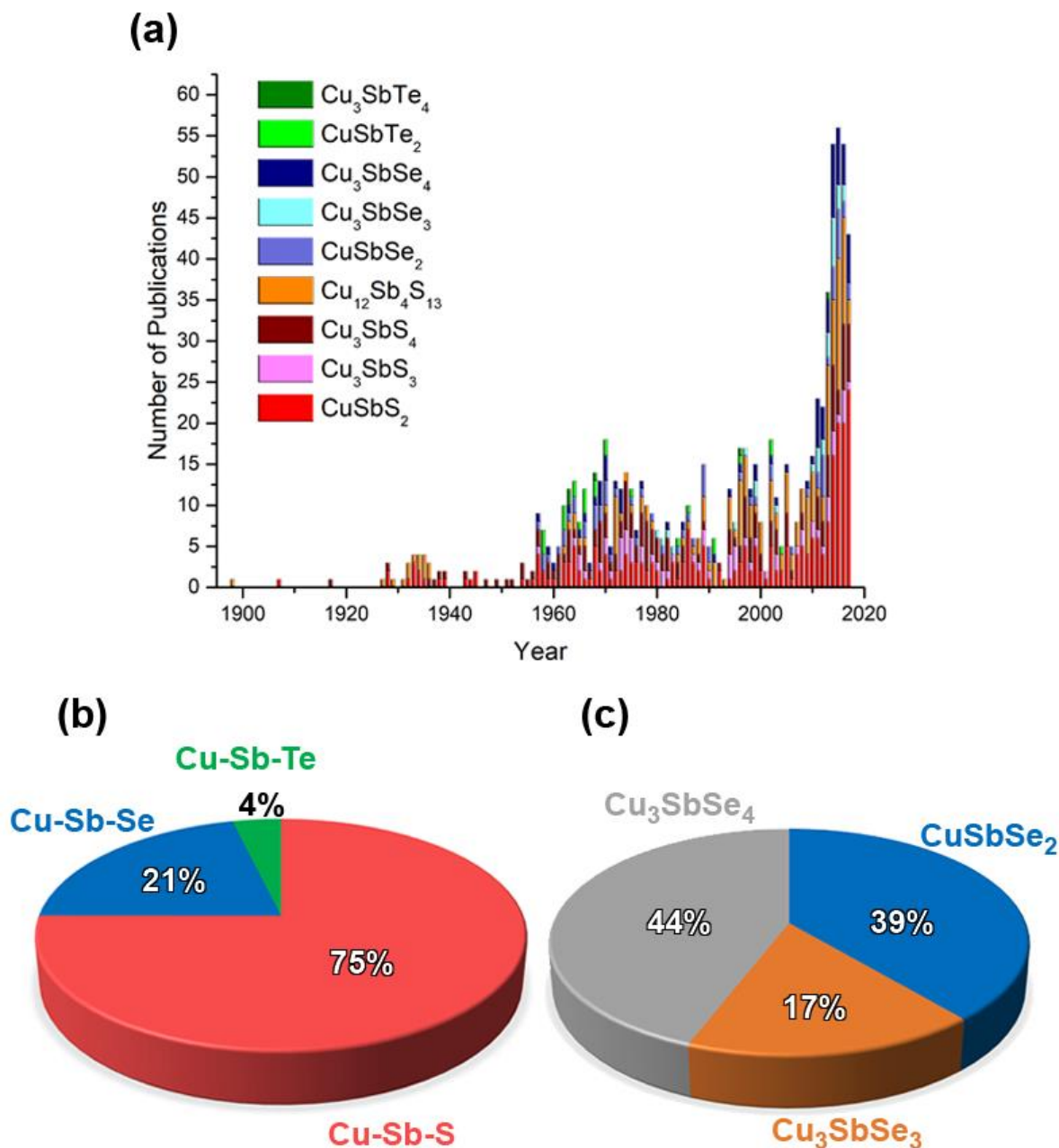


Figure 1.4 Publication record of Cu-Sb-Ch compounds: (a) history of Cu-Sb-Ch materials by species, (b) composition of Cu-Sb-Ch materials by anion, and (c) compositions of Cu-Sb-Se species by stoichiometry. There has been a surge in these compounds recently, though the majority of copper chalcogenidoantimonates have historically focused on the sulfides. It should, however, be noted that the data collected here for 2017 is incomplete as the year has not concluded. Telluride species are of little interest as the Cu-Sb-Ch family is often cited as an earth-abundant alternative to rare or toxic materials. Interestingly, all Cu-Sb-Se materials have experienced interest, though the majority of investigation of this family has revolved around thermoelectricity.

Cu_3SbS_3 crystallizes in the orthorhombic *Pnma* phase (SG #62). This material is found in the orthorhombic *Pnma* phase isostructural to the high temperature polymorph of Cu_3SbS_3 .⁵⁵

The *Pnma* phase of Cu_3SbCh_3 can be broken down into five irreducible positions, with one Sb, two Cu, and two Ch sites in the unit cell.^{50,56} There are planes of tilted corner-sharing CuSe_3 trigonal polyhedra perpendicular to the *c*-direction. Between these are SbSe_3 trigonal pyramids and CuSe_4 tetrahedra that share a common edge but connect to the network of CuSe_3 trigonal polyhedra at corners.

Interestingly, the *Pnma* phase is the only polymorph of Cu_3SbCh_3 that contains tetrahedral Cu. In contrast, both the $\text{P2}_1\text{2}_1\text{2}_1$ and $\text{P2}_1/\text{c}$ phases contain solely trigonal Cu and trigonal pyramidal Sb species, with each phase's connectivity defined by corner-sharing polyhedra. In fact, the lower symmetry $\text{P2}_1/\text{c}$ phase can be observed as two $\text{P2}_1\text{2}_1\text{2}_1$ unit cells in the *c*-direction, though half of the Cu atoms are displaced.

The last phase present in the Cu-Sb-S system is tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. Though not present as a selenium or tellurium analogue, this phase is best described similarly to Cu_3SbS_3 , with one Sb, and two unique positions for both the Cu and S. Belonging to the space group *I-43m* (SG #217), the unit cell is centered around a sulfur octahedrally bound to six CuS_3 trigonal polyhedra.⁵⁷ These polyhedra are further connected to two CuS_4 tetrahedra and a SbS_3 trigonal pyramid each, which comprise the majority of the framework. The structure is completed by three CuS_3 trigonal polyhedra at each vertex of the unit cell, and it bears mentioning that all polyhedra are connected via corner-sharing.

Copper antimony chalcogenides were observed as naturally-occurring minerals far before they were ever synthesized. The first recorded synthesis of any Cu-Sb-Ch compounds was reported by Wernick and Benson in 1957.⁵⁸ This work described synthesis, melting point, and crystal structure from X-ray diffraction data of CuSbS_2 , Cu_3SbS_3 , Cu_3SbS_4 , CuSbSe_2 , and Cu_3SbSe_4 . It should be noted that this work describes the

synthesized Cu_3SbS_3 as tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), but as having a cubic crystal structure (which is consistent with tetrahedrite). This structure resembles the structure of tetrahedrite, but with a void at the central sulfur atom, and may yield similar X-ray diffraction results. Therefore, the actual first synthesis of Cu_3SbS_3 would be in 1972 by Skinner et al.⁵⁹ Similarly, the first synthesis of Cu_3SbSe_3 was achieved in 1980 by Whitfield.⁵⁵

In addition to the three known phases of the Cu-Sb-Se system, there have been others proposed. Zhang et al. used DFT to predict several new compounds, but predominantly focused on Cu_4SbSe_5 , as well as a selenium analogue of the tetrahedrite phase at high temperatures.⁶⁰ The authors propose that the Cu_4SbSe_5 phase is only stable up to ~ 300 K, whereas $\text{Cu}_{12}\text{Sb}_4\text{Se}_{13}$ is stable at high temperatures, and is expected to be synthesized through a method similar to that reported for Cu_3SbSe_3 .⁶¹ The phase space of these compounds has been mapped,⁶²⁻⁶⁴ and several fundamental properties of these materials including ΔG° , ΔH° , and ΔS° have been identified.⁶⁵

A separate phase analysis work explored the phase formation and microstructure of a stoichiometric 3:1:3 (Cu:Sb:Se) quench from the melt.⁶⁶ Though annealing leads to phase-pure formation of Cu_3SbSe_3 under the conditions tested, it was determined that quenching from the melt produces a mixture of Cu_2Se , CuSbSe_2 , and Cu_3SbSe_3 which highlights the challenge of attaining phase-pure material for this system. Finally, conversion of the three-component product to phase-pure Cu_3SbSe_3 was also modelled successfully by Avrami kinetics.⁶⁶ Aside from crystallization, this work also reported values of elastic moduli and hardness for these materials.

Ternary phase formation has also been studied as a consequence of Cu addition to Sb_2Se_3 . This has been done through a chemical bath deposition wherein CuSe was deposited on top of a Sb_2Se_3 film followed by annealing.⁶⁷ Characterization of films as a function of bath time revealed its impact on electronic and optical properties (increasing electronic conductivity and decreasing band gap as the bath time increases, with phase pure Cu_3SbSe_4 obtained after 15 minutes). A separate study analyzed conversion of Sb_2Se_3 nanorods to Cu_3SbSe_3 nanorods by hot injection of Cu precursor wherein the aspect ratio of the rods was maintained.⁶⁸ Interestingly, this report also included observation of a localized surface plasmon resonance for the Cu_3SbSe_3 nanorods as identified by near-IR absorption, which has not been reported elsewhere.

Another study that has analyzed structural changes in the Cu-Sb-Se system was performed by Baker et al.⁶⁹ In this work, CuSbS_2 and CuSbSe_2 were subjected to pressures up to 80 GPa, and the resulting phase transformations were measured by high-pressure Raman spectroscopy and high-pressure X-ray diffraction (XRD). A phase change from orthorhombic *Pnma* to triclinic *P1* was observed at ~8 GPa. This transformation was completed at 13 GPa for CuSbS_2 and 10.2 GPa for CuSbSe_2 . These phase transformations were reversible upon release of pressure, but have implications for a more complex phase space in this system which may lead to new and exciting materials.

Not only is the phase space complex due to polymorphs under extreme conditions, but the ambient phases are also closely related. Both CuSbSe_2 and Cu_3SbSe_3 contain elements in the same oxidation states and as such are separated primarily by stoichiometry. On the other hand, Cu_3SbSe_4 contains an Sb^{5+} species with no lone pair, though the stoichiometry is similar to that of Cu_3SbSe_3 . These similarities contribute to difficulty in

the pure phase synthesis of any of these species. Aside from the ternary systems, there are also a variety of binary materials that can form, most commonly including CuSe, Cu₂Se, Sb₂Se₃. While balancing synthetic conditions to favor ternary phase formation has been established through a variety of methods (as will be discussed later in this review), avoiding impurity phase formation in this system is nontrivial and constitutes one of the larger challenges in investigation of fundamental properties of these materials.

In the following sections we will discuss the three Cu-Sb-Se materials with a focus on their application to thermoelectric energy generation. These will proceed by specific phases, beginning with Cu₃SbSe₄, continuing to Cu₃SbSe₃, and ending with CuSbSe₂. A comparison of thermoelectric figures of merit for the champion composition within each system can be found at the end of the section, in Table 1.3.

1.5 Cu₃SbSe₄ for Thermoelectrics

1.5a Doping

There are several methods to increase ZT. One of the most prominent includes doping, in order to change both thermal conductivity through phonon scattering, as well as electrical conductivity through the introduction of carriers.⁷⁰ There has been significant work performed on Cu₃SbSe₄ through this method, and with a variety of dopants.

In order to aptly select dopants and understand their effects on a material, knowledge of the native system is necessary. It is generally agreed that Cu₃SbSe₄ contains Cu⁺ and Se²⁻ species, though there is some disagreement as to the oxidation state of antimony. While native valence counting indicates the existence of Sb⁵⁺, some computational work instead suggest the presence of Sb³⁺ due to analysis of bandgap formation in this material.⁷¹ This

discrepancy is upheld experimentally through X-ray photoelectron spectroscopy (XPS). For Sb^{3+} to exist in this material, either Cu or Se must have multiple oxidation states ($\text{Cu}^+/\text{Cu}^{2+}$ or $\text{Se}^{2-}/\text{Se}_2^{2-}$) to maintain charge neutrality. However, most XPS studies show single environments for each constituent species,⁷²⁻⁷⁴ though it is noted that the binding energy of Sb is low which may cause ambiguity. Further, there is work claiming Sb^{3+} exists concurrently with Cu^+ and Cu^{2+} ,^{75,76} though these types of materials are observed to oxidize at the surface^{72,77} (as will also be demonstrated in chapter 2), which may be accountable for the observed oxidation states. Further support for the Sb^{5+} species in Cu_3SbSe_4 was obtained from a bond angle argument,^{78,79} XANES data,⁶¹ and rationalizing hole concentration as a function of dopant.⁸⁰ Due to this evidence, we propose that Cu_3SbSe_4 contains Cu^+ , Sb^{5+} , and Se^{2-} , though the low binding energy of Sb is of interest as its origin may cause the subtleties of the electronic structure.

Using this proposed valence counting, we may begin to understand and evaluate rational strategies for electronic structure doping approaches in the literature. Starting in 2011, Cu_3SbSe_4 was first doped with Sn on the Sb site.⁸¹ It was hypothesized that Sn^{4+} doping onto a Sb^{5+} site would serve as a hole dopant to improve carrier concentration, and by extension the thermoelectric figure of merit. In fact, Sn-doping of Cu_3SbSe_4 is the most popular method, as employed in several studies.⁸⁰⁻⁸⁵ The inclusion of Sn^{4+} serves as a p-type dopant by pinning the Fermi level to the valence band maximum, and providing disperse states at VBM which leads to a low effective hole mass. This acts in conjunction with the measured increase of the hole concentration despite decreasing the hole mobility slightly,^{80,81} as the effect of the carrier concentration is stronger and is reflected in the up to tenfold increase in electronic conductivity.⁸¹ This improvement in electronic structure

combined with the decrease observed in thermal conductivity attributed to phonon scattering to yield ZT as high as 1.05 at 690 K.⁸³

Further improvements were made in this system by substituting the chalcogenide site with S for Se.^{82,86} Typically, in thermoelectric materials Se is substituted by Te, though in keeping with the desire for earth-abundant alternatives to high-efficiency thermoelectrics, sulfur is the more attractive choice. Doping with another chalcogenide was chosen due to the small electronegativity difference of S²⁻ and Se²⁻ which might help to conserve carrier mobility, while utilizing differences in atomic mass and ionic radius to promote phonon scattering. Interestingly, as sulfur incorporation for Cu₃Sb(Se_{1-x}S_x)₄ increases to x=0.5, both the hole mobility as well as the thermal conductivity decrease. This can be reconciled with the lower electronic conductivity of Cu₃SbS₄ relative to Cu₃SbSe₄,⁵¹ and the distortion of the lattice that may improve phonon scattering. Further, codoping both Sn on Sb sites with S on Se sites was used to increase the ZT for this system up to 1.1 at 673 K.⁸²

A variety of dopants have been explored for Cu₃SbSe₄. Typically, these elements are chosen for their ability to improve p-type character of the material and include Sn,^{80,81,83-85} Ge,^{85,87} Bi,⁸⁸ Al,^{89,90} In,⁹⁰⁻⁹² As,⁹³ Ga,^{90,94} Zn,⁹⁵ S,⁸⁶ and Te.⁹⁶ The results of these materials can be seen in Table 1.1. While As and Bi are chosen for their electronic similarities to Sb, other elements such as Al, Ga, Ge, Sn, and Zn were chosen for their ability to hole-dope the material. Similarly, the effect of substoichiometric Cu was also elucidated^{72,97} and determined to act as a hole dopant to account for the p-type nature of Cu₃SbSe₄. Interestingly, doping with some extrinsic species such as Sn,^{80,81,83-85} and Ge⁸⁵ render Cu₃SbSe₄ a degenerate semiconductor whereas Ga,^{90,94} Bi⁷³ and Zn⁷⁴ do not affect

Table 1.1 Thermoelectric properties of Cu_3SbSe_4 and its doped species. Properties detailed are those for the highest reported ZT. MA/SPS synthesis was performed by mechanical alloying followed by spark plasma sintering.

Material	Site	Synthesis	ZT _{max}	Reference
Cu_3SbSe_4	N/A	Coprecipitation	0.62 at ~660 K	83
$\text{Cu}_3\text{Sb}_{0.98}\text{Sn}_{0.02}\text{Se}_4$	Sn _{Sb}	Coprecipitation	1.05 at 690 K	83
$\text{Cu}_3\text{Sb}_{0.94}\text{Sn}_{0.06}\text{Se}_{3.5}\text{S}_{0.5}$	Sn _{Sb} , S _{Se}	Coprecipitation	1.1 at 700 K	82
$\text{Cu}_3\text{As}_{0.5}\text{Sb}_{0.5}\text{Se}_4$	As _{Sb}	Hot Injection	N/A	93
$\text{Cu}_3\text{Sb}_{0.98}\text{Bi}_{0.02}\text{Se}_4$	Bi _{Sb}	Hot Injection	0.81 at 648 K	88
$\text{Cu}_3\text{Sb}_{0.88}\text{Sn}_{0.10}\text{Bi}_{0.02}\text{Se}_4$	Sn _{Sb} , Bi _{Sb}	Hot Injection	1.26 at 673 K	73
$\text{Cu}_3\text{Sb}_{0.97}\text{Ge}_{0.03}\text{Se}_{2.8}\text{S}_{1.2}$	Ge _{Sb} , S _{Se}	Direct melting	0.89 at 650 K	87
$\text{Cu}_{2.98}\text{SbSe}_4$	V _{Cu}	Direct melting	0.59 at 650 K	97
$\text{Cu}_{2.5}\text{Zn}_{0.5}\text{SbSe}_4$	Zn _{Cu}	Direct melting	0.35 at 475 K	74
$\text{Cu}_3\text{Sb}_{0.995}\text{Al}_{0.005}\text{Se}_4$	Al _{Sb}	Direct melting	0.88 at 623 K	90
$\text{Cu}_3\text{SbS}_{0.5}\text{Se}_{3.5}$	S _{Se}	Direct melting	N/A	86
$\text{Cu}_{2.95}\text{Sb}_{0.96}\text{Ge}_{0.04}\text{Se}_4$	Ge _{Sb} , V _{Cu}	Direct melting	0.7 at 640 K	99
$\text{Cu}_3\text{SbSe}_{3.99}\text{Te}_{0.01}$	Te _{Se}	Direct melting	0.62 at 623 K	96
$\text{Cu}_3\text{Sb}_{0.995}\text{In}_{0.005}\text{Se}_4$	In _{Sb}	Direct melting	0.88 at 623 K	90
$\text{Cu}_3\text{Sb}_{0.995}\text{Ga}_{0.005}\text{Se}_4$	Ga _{Sb}	Direct melting	0.90 at 623 K	90

the intrinsic Cu_3SbSe_4 nondegenerate (or partially degenerate) status. The conversion to a degenerate status is likely due to the proximity of the Fermi energy to the valence band.^{73,98}

A final distinction about the doping of Cu_3SbSe_4 should be made. While Zn and As have been included in this compound, the concentrations of these constituents are high enough that these may be more appropriately considered as solid solutions. Interestingly, for the case of Zn inclusion no phase-pure $\text{Cu}_{3-x}\text{Zn}_x\text{SbSe}_4$ was reported, as all doped samples were accompanied by the presence of a CuSbSe_2 phase.⁹⁵ Also, with a high level of Zn inclusion, interesting observations about substitution were made. Primarily, it was determined that the optimal thermoelectric properties for this system were found with the

stoichiometry $\text{Cu}_{2.5}\text{Zn}_{0.5}\text{SbSe}_4$, as for $\text{Cu}_2\text{ZnSbSe}_4$ Zn sits on all Cu1 sites leading to no asymmetry that would reduce thermal conductivity.

While these varieties of doped materials are capable of achieving ZT higher than intrinsic Cu_3SbSe_4 , none have been capable of matching the value of 1.1 set by the Sn- and S-codoped sample.⁸² However, using a similar approach as the Sn- and S-codoped sample, Liu et al. reported codoping Cu_3SbSe_4 using both Bi and Sn on Sb sites.⁷³ As shown in figure 1.5, they found that Bi-doping leads to higher electronic resistivity which is attributed to the compensation of charge by V_{Se} . Simultaneously, Bi-doping increases the Seebeck coefficient with respect to the undoped Cu_3SbSe_4 , due to the reduced effective mass of electrons in the doped sample. The other element used to dope the sample, Sn, was found to lower the Fermi energy within the valence band resulting in a degenerate

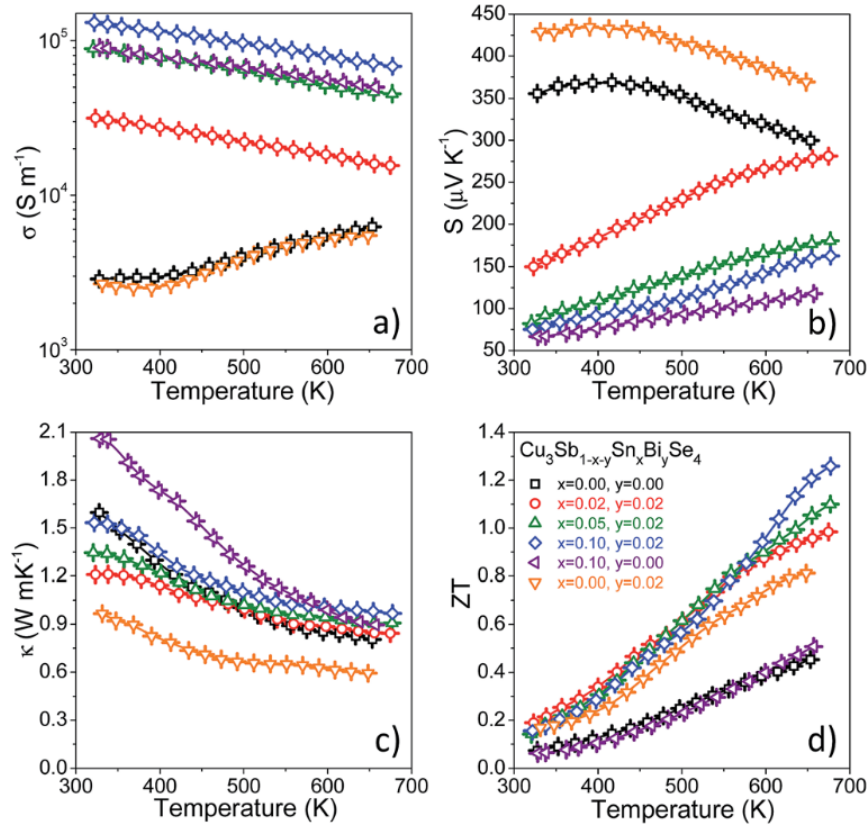


Fig. 1.5 Temperature dependence of (a) electric conductivity (σ), (b) Seebeck coefficient (S), (c) thermal conductivity (κ), and (d) TE figure of merit (ZT) of $\text{Cu}_3\text{Sb}_{0.98-x}\text{Sn}_x\text{Bi}_{0.02}\text{Se}_4$. The $\text{Cu}_3\text{Sb}_{0.88}\text{Sn}_{0.10}\text{Bi}_{0.02}\text{Se}_4$ composition exhibits the highest ZT value of all Cu_3SbSe_4 materials to date. Reproduced from reference 73.

semiconductor. In order to optimize both charge carrier concentration and band structure simultaneously, the Cu_3SbSe_4 was codoped with both Bi and Sn on Sb sites. Codoped samples exhibit lower electrical resistivities and higher Seebeck coefficients than purely Sn-doped Cu_3SbSe_4 . The maximum ZT of 1.26 at 673 K was obtained for this system for the sample with the stoichiometry $\text{Cu}_3\text{Sb}_{0.88}\text{Sn}_{0.10}\text{Bi}_{0.02}\text{Se}_4$. The authors of this study also built a ring thermoelectric generator, which is capable of generating > 1 mW of power for each thermoelectric element for a temperature up to 160 °C, with an open circuit potential close to 20 mV.

Aside from this example of the practicality of these materials, theoretical work has been performed to identify optimal dopants and to improve our understanding of the electronic structure of Cu_3SbSe_4 .⁹⁸ This thorough study provides the basis for future work in identifying appropriate dopants to further optimize thermoelectric function in Cu_3SbSe_4 materials. A basic summary reveals that symmetry and local coordination are critical to the electronic structure and function of this species. While the p-type character of intrinsic Cu_3SbSe_4 is attributed to V_{Cu} , extrinsic dopants have the ability to tune a variety of properties in this material. Doping Cu_3SbSe_4 n-type can be feasibly achieved by substituting Mg or Zn on a Cu site, or I on a Se site. For p-type doping, Na_{Cu} is the most promising option for the Cu site while no feasible dopant was found on the Se site (which may be due to the local coordination symmetry of the Se environment). However, the most versatile crystallographic identity for doping is Sb, where Ti_{Sb} is the predicted best dopant due to its ability to provide lattice mismatch without significantly altering the band structure. Finally, despite many of these possible dopants having positive formation

energies, it is suggested that these may be overcome through appropriate synthetic methods controlling temperature and employing kinetic control.

As we have detailed above, a wide variety of dopants have been explored for Cu_3SbSe_4 . However, synthesis conditions have varied greatly between experiments. Reports of Cu_3SbSe_4 have spanned synthetic routes such as direct melting,^{49,51,74,81,85-90,92,96,99-102} one pot,^{76,82,83} hot injection,^{73,84,93} microwave,^{75,91} chemical bath,⁶⁷ and mechanical alloying routes.^{72,80} Post-synthesis, pellets are typically pressed but even here different methods have been applied, though Li et al. have reported the effects of select hot-pressing conditions.⁸³ Aside from hot-pressing, Cu_3SbSe_4 has also undergone densification by annealing in a selenium-rich environment⁹³ and spark-plasma sintering.⁸⁸ There has not yet been a thorough comparison of these different methods and their effects on thermoelectric function in Cu_3SbSe_4 .

Another aspect that is often overlooked in Cu_3SbSe_4 reporting is the impact of grain size. While it is largely accepted that grain size is inversely related to phonon scattering (and by extension, reduction of thermal conductivity), the active material must be carefully considered. For example, as nanoscaled thermoelectric materials are desirable as low-dimensional materials,¹⁷ Cu_3SbSe_4 has been synthesized on the nanoscale via several methods as will be detailed in section 1.5b. However, the surfaces of these nanocrystals are often passivated with organic ligands. Without removal of these ligands, low densities are achieved.⁸⁴ However, Liu et al. showed that using ammonium thiocyanate, they could remove the organic ligands and achieve densities of ~90% of the theoretical value by hot pressing pellets.⁷³

Another issue with comparison of thermoelectric function in these different materials is the temperature at which thermoelectric properties are reported. As observed in almost all ZT data for Cu_3SbSe_4 , the figure of merit increases as temperature increases, though no levelling off point has been observed, which means the figure of merit is likely limited by the melting point of Cu_3SbSe_4 (734 K)⁷² and there is no single optimum temperature to report a ZT_{max} in order to compare these materials. It is also crucial to consider melting point depression as a balance between temperature of measurement for maximum ZT versus the grain size as the material is nanoscaled. Therefore, we propose that while reporting the maximum ZT is still encouraged, thermoelectric measurements should be performed and reported at 673 K to provide a reasonably high temperature for thermoelectric function but avoid issues with material decomposition. This may help to achieve large ZT values for Cu_3SbSe_4 , while providing a point of comparison between different works. Further, this temperature is chosen to be significantly lower than the melting point of Cu_3SbSe_4 to avoid complications with the onset of melting, and 673 K is a temperature amenable to measurement on a range of instrumentation.

Experimental data demonstrates that for the highest efficiency thermoelectric Cu_3SbSe_4 materials, Sn-doping is a critical component, as the only instances of Cu_3SbSe_4 devices with a $\text{ZT} > 1$ all involve Sn-doping.^{73,82,83} In all these cases, Sn^{4+} dopes on a Sb^{5+} site, where it acts as a hole dopant while preserving the similar electronic structure of Sb^{5+} . Similarly, Ti^{4+} was hypothesized to be a more effective dopant than Sn^{4+} due to the larger predicted thermopower in the former.⁹⁸ While other species mimicking Sb^{5+} in groups 13-15 have been explored, other earth-abundant opportunities have been ignored such as Ga^{3+} which may be more similar to Sb^{5+} electronically than Al^{3+} but retain the strong mass

fluctuations necessary for phonon scattering, suggesting it may succeed where the latter failed to produce ZT higher than 0.58.⁸⁹

To further this direction, the highest thermoelectric figures of merit have been reached using a codoping technique.^{73,82} However, while an excellent in-depth analysis of dopant effects for Cu_3SbSe_4 exists, the impact of codopants together has been largely unexplored. As we have observed with the maximal ZT values obtained through this method, it holds the most promise for tailoring properties of the system in the future.

1.5b Nanoscaling

Thermoelectrics function as a combination of both electronic and thermal carrier transport. Defect analysis primarily investigates variations in the electronic band structure. However, complementary improvements to thermoelectric function can be obtained by also focusing on thermal transport. One of the major movements in thermoelectrics has been to provide increased phonon scattering (thereby decreasing thermal conductivity) at grain boundaries by employing “low-dimensional” materials.^{17,103-105}

To accomplish low dimensional Cu_3SbSe_4 , a variety of methods have been tested for synthesis on the nanoscale, including coprecipitation,⁸² microwave,⁷⁵ self-organized arrested precipitation,⁷⁶ and hot injection.^{73,84,93} These many different methods yield particles of varying sizes (figure 1.6), all with varying properties. Despite this variety of nanocrystalline Cu_3SbSe_4 , the observed effects of dopants on the bulk parent compound are also reflected in doped nanocrystalline samples.

While it is widely agreed upon that nanoparticles can serve to increase ZT of a material, it becomes important to inspect the differences in particles produced through the

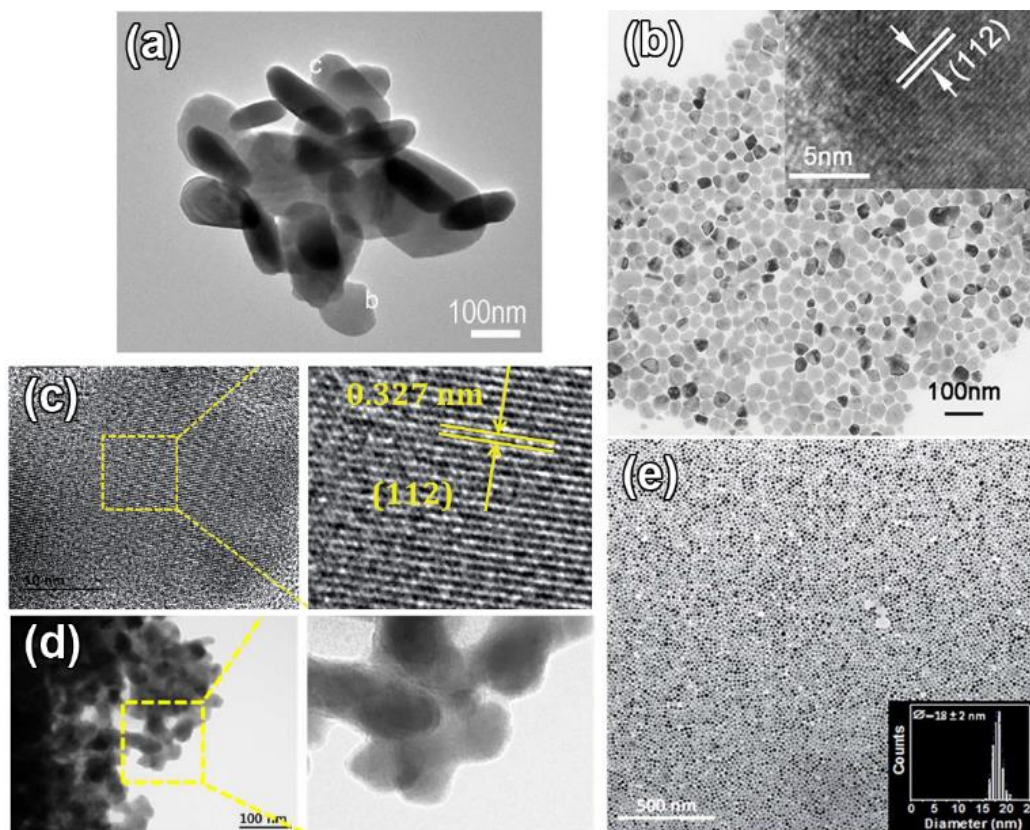


Figure 1.6 Transmission electron microscopy images of various Cu_3SbSe_4 nanocrystals as synthesized by a) coprecipitation (reference 83), b) hot injection (reference 84), c) microwave (reference 75), d) self-organized arrested precipitation (reference 76), e) hot injection (reference 73)

different methods to compare and contrast properties of the resulting products while acknowledging the feasibility of each method for cost, control, and scalability.

The results of the different synthetic methods are shown in Table 1.2. While it can be seen that high ZT values have been achieved with nanocrystalline Cu_3SbSe_4 synthesized using both coprecipitation and hot injection routes, the resulting products exhibit similar thermoelectric properties. Therefore, the discussion about different syntheses should focus on the resulting differences in the materials produced.

For example, solution-based synthetic routes are often desirable for the high degree of control they afford over product properties such as particle size, morphology, and dispersity. However, these routes often utilize coordinating organic media to achieve this synthetic control. These organic ligands are often detrimental to thermoelectric function,

Table 1.2 Comparison of Cu₃SbSe₄ nanocrystalline products. Note: properties given are measured at the temperature of ZT_{max} unless otherwise specified, with the exception of density (measured at room temperature, percentages given relative to theoretical maximum). Particle sizes are reported as-synthesized, before any sintering or annealing

Material	Synthesis	Particle size (nm)	Processing	Density (gcm ⁻³)	σ ($\Omega^{-1}\text{cm}^{-1}$)	κ (Wm ⁻¹ K ⁻¹)	ZT	Reference
Cu ₃ SbSe ₄	Hot Injection	35	Hot-pressed 1 hr at 350 °C	4.84		0.91		84
Cu ₃ Sb _{0.98} Sn _{0.02} Se ₄	Hot Injection	35	Hot-pressed 1 hr at 350 °C	4.92		1.1	0.5 at 575 K	84
Cu ₃ As _{0.5} Sb _{0.5} Se ₄	Hot Injection	~100	Sintered in a 100 Torr Se environment 30 minutes at 340 °C		6			93
Cu ₃ SbSe ₄	Microwave	25	Annealed 1 hr at 177 °C		345	0.166	0.141 at 300 K	75
Cu ₃ SbSe ₄	Self-organized arrested precipitation	40 (after annealing)	Annealed 1 hr at 200 °C		723.84	0.478	0.2 at 300 K	76
Cu ₃ SbSe ₄	Coprecipitation	100-200 platelets and 50 x 150 nm rods	Hot-pressed at 275 °C under 600 MPa for 1 hr	5.30-5.66	29.4	~0.6	0.62 at 690 K	83
Cu ₃ Sb _{0.98} Sn _{0.02} Se ₄	Coprecipitation	30-50 x 200 rods	Hot-pressed at 350 °C under 600 MPa for 1 hr	5.30-5.66	645	~1.0	1.05 at 690 K	83
Cu ₃ Sb _{0.94} Sn _{0.06} Se _{3.5} S _{0.5}	Coprecipitation	43.4	Hot-pressed at 350 °C under 600 MPa for 1 hr	~89%	1250 at 298 K	~1.7	1.1 at 700 K	82
Cu ₃ SbSe ₄	Hot Injection	18	Hot-pressed at 380 °C, 70 MPa, 30 min	~90%	29 at 298 K	0.81	~0.45 at 648 K	73
Cu ₃ Sb _{0.98} Sn _{0.02} Se ₄	Hot Injection	18	Hot-pressed at 380 °C, 70 MPa, 30 min	~90%	454 at 298 K	~0.8	0.97 at 673 K	73
Cu ₃ Sb _{0.98} Bi _{0.02} Se ₄	Hot Injection	18	Hot-pressed at 380 °C, 70 MPa, 30 min	~90%	26 at 298 K	~0.6	0.81 at 648 K	73
Cu ₃ Sb _{0.88} Sn _{0.1} Bi _{0.02} Se ₄	Hot Injection	18	Hot-pressed at 380 °C, 70 MPa, 30 min	90%	1309	~1.0	1.26 at 673 K	73

especially in decreasing electronic conductivity. This has led to a variety of methods to circumvent this issue, many of which have been applied to the Cu_3SbSe_4 system.

The most straightforward approach conceptually is to remove the organic ligands via a ligand exchange procedure. This was performed on $\text{Cu}_3\text{Sb}_{1-x-y}\text{Sn}_x\text{Bi}_y\text{Se}_4$ nanocrystals, wherein NH_4SCN was used to supplant the native oleylamine from the surface, rendering the material more electronically conductive.⁷³ Without a ligand exchange, Cu_3SbSe_4 nanocrystals are observed to exhibit low density.⁸⁴ This is important as density has been shown to impact thermoelectric function.¹⁰⁶

Hot-pressing is the most common step to densifying Cu_3SbSe_4 nanomaterials. Despite its ubiquity, there is no generally agreed upon set of conditions for hot-pressing to achieve an optimal pellet, with procedures for Cu_3SbSe_4 densification ranging from hot pressing pressures of 70 MPa⁷³ to 600 MPa.⁸² When considering hot pressing nanomaterials, it is important to consider these experimental parameters as hot pressing may lead to grain growth. While this may lead to an improvement in electronic transport properties, it also reduces the beneficial thermal conductivity reduction resulting from nanostructuring. Parameters involved with hot pressing include temperature and time, and all of these criteria are important to consider when searching for optimum densification conditions. To this end, Li et al.⁸³ tested several different hot-pressing conditions, and determined that the best condition of those tested was at 275 °C for 1 hour (all samples were processed using a pressure of 600 MPa) as observed in Figure 1.7. Longer hot-pressing times and higher temperatures were found to increase electronic conductivity. This is attributed to both an increase in grain size as well as increase in the carrier concentration due to V_{Se} .¹⁰⁷ Further, the sample hot-pressed for 30 minutes exhibits

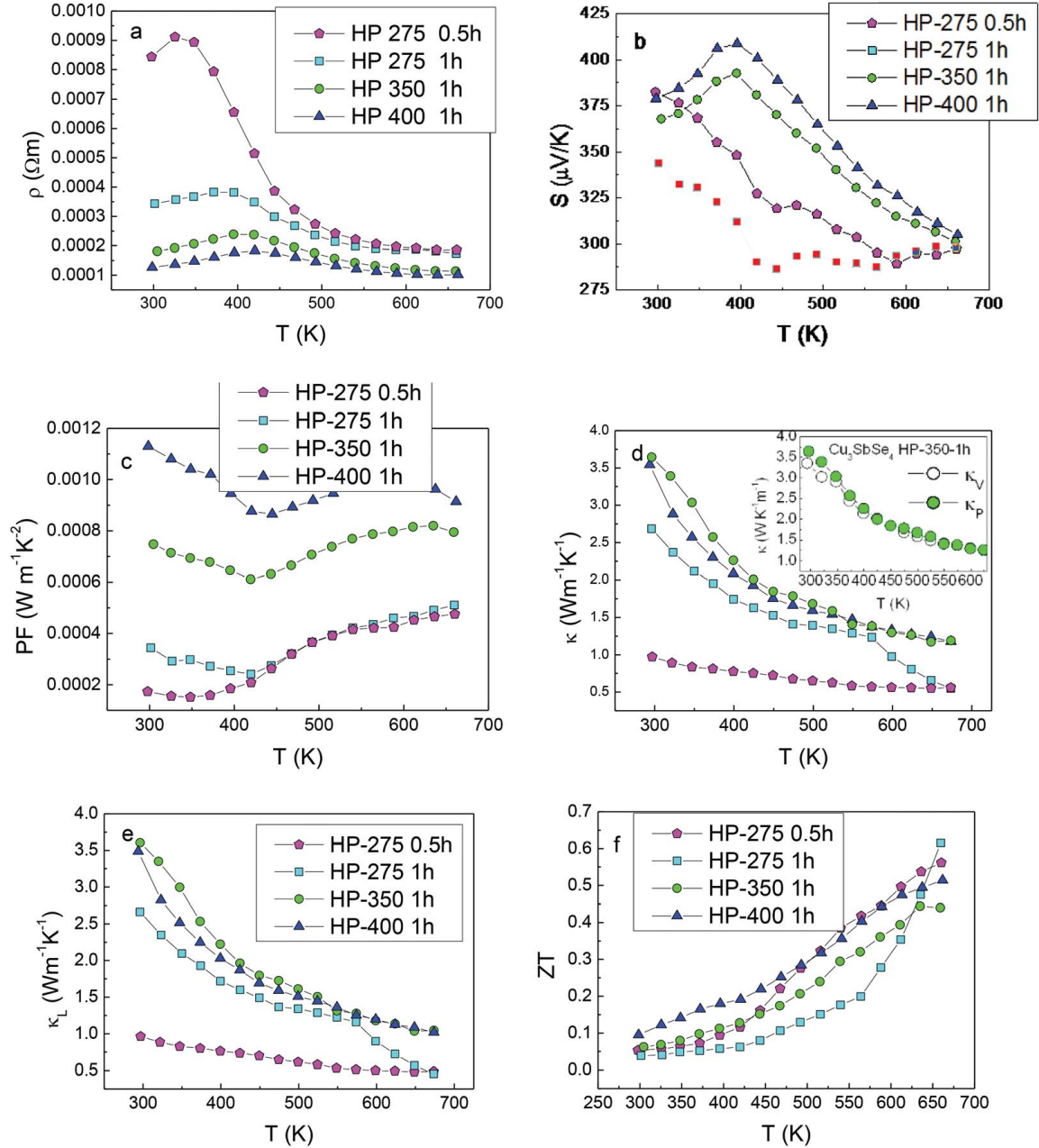


Figure 1.7 Temperature dependence of: a) electric resistivity (ρ), b) Seebeck coefficient (S), c) power factor (PF), d) thermal conductivity (κ), e) lattice thermal conductivity (κ_L), f) figure of merit (ZT) of Cu_3SbSe_4 nanocrystals compacted using different hot-pressing temperatures and times. Inset of d): thermal conductivity of Cu_3SbSe_4 -HP-350 in the directions parallel to the pressing direction (κ_p) and vertical to the pressing direction (κ_v). From reference 83.

significantly lower thermal conductivities than the sample hot-pressed for 60 minutes.

This may indicate the incompleteness of densification by failure to remove ethylenediamine from the surface as this would effectively scatter phonons strongly (especially mid- and long-range phonons which can transport heat effectively in bulk samples but are scattered

in nanoscale samples). Unfortunately, the lowest temperature studied here demonstrated the best thermoelectric results, and so further testing should ideally be provided to elucidate colder temperatures as well as varying the hot-pressing pressure and temperature to ensure the densification proceeds to completion.

Hot-pressing is of interest not only for its ubiquity, but also from the perspective of surface analysis. The high temperatures employed in hot-pressing pellets may be sufficient to remove organic ligands from the surface of as-synthesized nanocrystals. Further, as we have just revealed, hot-pressing may lead to changes in surface chemistry with increase in carrier concentration attributed to formation of a Se-poor surface.⁸³ This Se-poor surface may impart additional electronic states whose impact on thermoelectric function is unknown. Further, surfaces play a role in both electronic properties of nanocrystalline materials²⁹ as well as incorporation of dopant or defect states.¹⁰⁸ Therefore, some work remains to elucidate the full effect of surface chemistry in nanocrystalline Cu_3SbSe_4 , for both the effects of grain growth and ligand loss through hot-pressing, or the passivation of beneficial dopants at the surface of this species.

One method to address this Se-poor surface was the use of sintering in a Se-rich environment.⁹³ This was determined to densify particles and enlarge domain sizes. Post-synthetic treatments like this are critical to improving electronic properties of the nanocrystalline materials, however they typically involve high-temperature steps. As noted in section 1.5a, these high temperatures may be beneficial to thermoelectric performance, as the figure of merit for Cu_3SbSe_4 increases with temperature. However, nanoscale Cu_3SbSe_4 demonstrates a reduction in lattice thermal conductivity of 73% over bulk Cu_3SbSe_4 due to scattering of mid- and long-range phonons that still transport heat in bulk

materials.⁸³ Unfortunately, the high temperature processing involved in densification and thermoelectric testing leads to grain growth and may adversely affect nanoscale materials significantly more than bulk samples, especially as nanocrystalline solids experience a melting point depression¹⁰⁹ which may decompose materials before their maximum ZT is achieved.

While the record ZT for this system has been set using Sn- and Bi-codoped Cu_3SbSe_4 nanocrystals, several considerations must be taken on the nanoscale. First, the surface of the particles becomes significantly more important to carrier transport, specifically due to the higher surface area-to-volume ratio in nanocrystalline materials. Second, defect passivation and introduction of electronic surface states may play a role in these materials, though they have not yet been investigated thoroughly. Densification methods yield promising results for thermoelectric function in this system, with hot-pressing a pellet using cool temperatures with long pressing times yielding the best results (though we recommend more work to better understand the effects of pressing temperatures and the effect of pressing pellets on material surface properties). Finally, a balance of particle size¹⁷ and temperature is encouraged to optimize phonon scattering of a broad range of wavelengths while retaining device function due to phase decomposition at high temperatures (i.e. melting). Aside from the record figures of merit achieved for nanocrystalline samples, they also provide perfect scaffolds to explore the surface effects in thermoelectric materials due to their large surface-to-volume ratio and accurate reflection of bulk properties.

1.5c Nanoinclusion Composites

While doping on the atomic scale has been well-characterized and demonstrated to increase ZT by improving carrier transport or reducing thermal conductivity, other length-scales have also been explored. As shown in figure 1.8, rational design strategies employing hierarchical structures on the nano- and mesoscale can further improve ZT.¹¹⁰ This approach, when rationally performed and employing electronic state matching, can drastically lower thermal conductivity by broad-based phonon scattering while maintaining a high power factor.

Therefore, while Cu_3SbSe_4 has been analyzed for its thermoelectric properties in the bulk and on the nanoscale, it has also been applied in this context. Similar to its use as a nanocrystalline material, Cu_3SbSe_4 has also been employed as nanoinclusions in bulk matrices of other high-ZT materials. In these instances, the majority of the thermoelectric

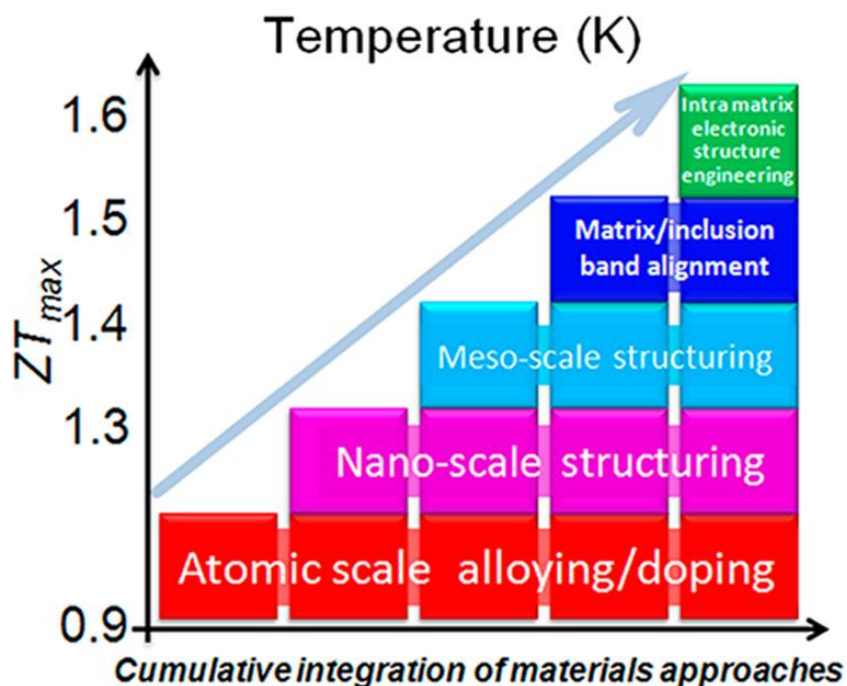


Figure 1.8 Integration of material approaches as a function of ZT. Adapted from reference 110.

behavior comes not from Cu_3SbSe_4 , but it instead acts as a scattering center to improve the overall efficiency of the material.

In matrix/nanoinclusion composite systems, Cu_3SbSe_4 has been shown to improve the thermoelectric figure of merit higher than the matrix alone. Samples were fabricated by direct fusion of the matrix material ($\beta\text{-Zn}_4\text{Sb}_3$ ¹¹¹ or $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ¹¹²), followed by solvothermally synthesizing Cu_3SbSe_4 ⁸³. These products were milled together to achieve bulk grains of the matrix and ~ 200 nm nanoinclusions of Cu_3SbSe_4 .

In these composite materials, Cu_3SbSe_4 acts as a hole injector via a type I p-p heterojunction, as seen in figure 1.9. Here, holes are injected from the larger bandgap material (nanoinclusion Cu_3SbSe_4) into the smaller bandgap material (matrix). The resulting effective barrier height acts as a scatterer through the energy filtering effect.¹¹³ The increased amount of scattering greatly affects thermal conductivity, as both grain boundaries and phase boundaries affect phonon propagation, while the significantly larger volume fraction of grain boundaries preserves carrier mobility.

However, this is where the similarities between these two studies ends. Unlike intrinsic Cu_3SbSe_4 , the Seebeck coefficient of the matrices increases to a point before decreasing, which is attributed to contributions from thermally promoted minority carriers.

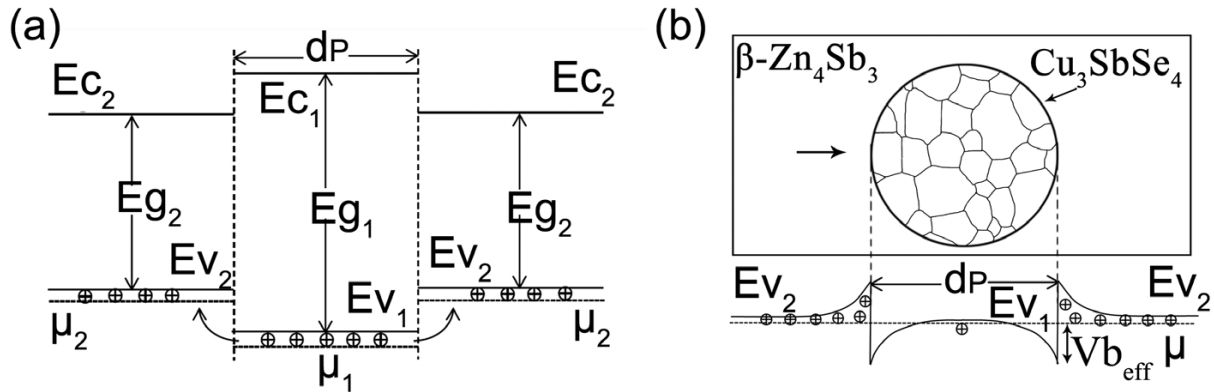


Figure 1.9. Depiction of energy level alignment in a Cu_3SbSe_4 (inclusion)- $\beta\text{-Zn}_4\text{Sb}_3$ (matrix) composite: a) before contact, and b) p-p type interface potential barriers with effective barrier height $V_{b_{\text{eff}}}$ formed from band bending. Adapted from reference 111.

This is also observed in other small bandgap materials like AgSbTe_2 ,¹¹⁴ as well as nanoincorporation composites.¹¹⁵ Addition of Cu_3SbSe_4 nanoinclusions to $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alter this such that the Seebeck coefficient increases with temperature almost monotonically, which may suggest the inclusion of Cu_3SbSe_4 more effectively scatters minority carriers. However, for the $\beta\text{-Zn}_4\text{Sb}_3$ case, the inclusion of Cu_3SbSe_4 does not appear to affect the Seebeck coefficient significantly.

The other interesting difference between these two systems is the concentration of nanoinclusions necessary to obtain the maximum ZT. The optimal conditions for maximizing the figure of merit in $\beta\text{-Zn}_4\text{Sb}_3$ involves 5 vol% Cu_3SbSe_4 , reaching a high of $\text{ZT} = 1.37$ at 648 K which is near double that of the intrinsic matrix from this study, and is higher than the record $\text{ZT} = 1.3$ obtained for $\beta\text{-Zn}_4\text{Sb}_3$ alone.¹⁰ To the contrary, the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ study determined that the minimal amount of Cu_3SbSe_4 was preferable. Here, 1 vol% Cu_3SbSe_4 was used to obtain a maximum ZT of 1.6 at 476 K, which is ~22% larger than that of nanocrystalline $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (1.4 at 373 K).¹¹⁶

While nanoinclusions involving Cu_3SbSe_4 can clearly been seen to improve thermoelectric function of a matrix material alone, no works exist that utilize Cu_3SbSe_4 as the matrix material. Having achieved a ZT of 1.26,⁷³ it is possible that nanoinclusions may be utilized to improve scattering in this material and increase the figure of merit further. Also, the concept of hole injection may serve to supplant some of the function of dopants, adding to the applicability and versatility of the Cu_3SbSe_4 system. Despite the promise of this method, the scarcity of results exploring the use of Cu_3SbSe_4 as a nanoinclusion for thermoelectric applications limits our working knowledge, but the promising results indicate that this approach warrants further investigation.

1.6 Cu₃SbSe₃ for Thermoelectrics

Another compound that has been explored for thermoelectric applications is Cu₃SbSe₃. A semiconductor like Cu₃SbSe₄, Cu₃SbSe₃ also exhibits p-type conductivity, though the values of ZT achieved for this material are significantly lower than those of Cu₃SbSe₄. Regardless, Cu₃SbSe₃ is of considerable interest for thermoelectric applications due to its ultralow thermal conductivity (as low as 0.26 Wm⁻¹K⁻¹).¹¹⁷

This anomalous thermal conductivity is a product of the anharmonicity in this material. In turn, the anharmonicity is a product of three related phenomena, which will be described in the coming sections: chemical bonding, lone pair effects, and an order/disorder transition.

1.6a Chemical Bonding

There are several significant differences between Cu₃SbSe₃ and Cu₃SbSe₄ with respect to the structure and function of these materials. As detailed above, Cu₃SbSe₄ possesses a highly symmetric structure, comprised of corner-sharing CuSe₄ and SbSe₄ tetrahedra.⁴⁹ On the contrary, Cu₃SbSe₃ is a more complex structure⁵⁰ containing two Cu and two Se environments, with an overall lower degree of structural symmetry. This is expected to lead to a lower thermal conductivity in Cu₃SbSe₃ than Cu₃SbSe₄.¹¹⁸ However, this complex structure alone is not sufficient to describe the low thermal conductivity in Cu₃SbSe₃.

Next, a bonding model in the material should be considered. Chemical bond hierarchy is observed in Cu₃SbSe₃, with Sb and Se exhibiting a rigid sublattice while Cu is more weakly bonded. This leads to a state of a “part-crystalline part-liquid” material.¹¹⁹ In

this case, the atomic displacement parameters for Cu are very large and fluid-like mobility of the Cu is calculated (Figure 1.10).

This fluid-like mobility of Cu in Cu_3SbSe_3 is necessary for accurately modelling experimentally-obtained thermal conductivity data.⁶¹ In a comparison of Cu_3SbSe_4 , Cu_3SbSe_3 , and CuSbSe_2 , the lattice thermal conductivity of Cu_3SbSe_3 is anomalously low, and almost temperature-independent.¹²⁰ Further, while the thermal conductivity behavior of Cu_3SbSe_4 and CuSbSe_2 may be fit with Normal and Umklapp scattering, in order to fit the Cu_3SbSe_3 data an additional rattling-like term was necessary. The rattling-like term is considered by removing some of the contribution from fluid-like Cu.

The fluidlike characteristic of Cu_3SbSe_3 at raised temperatures may help explain some of its attractive thermoelectric properties. While arguments have been made to suggest that the anharmonicity attributed to lone pairs present on Sb are sufficient to describe the minimal thermal conductivity present in this material (as will be discussed in the following section, 1.6b), fluidlike character in the Cu sublattice of Cu_3SbSe_3 serves to effectively scatter phonons. Further, this property is not limited to interest for

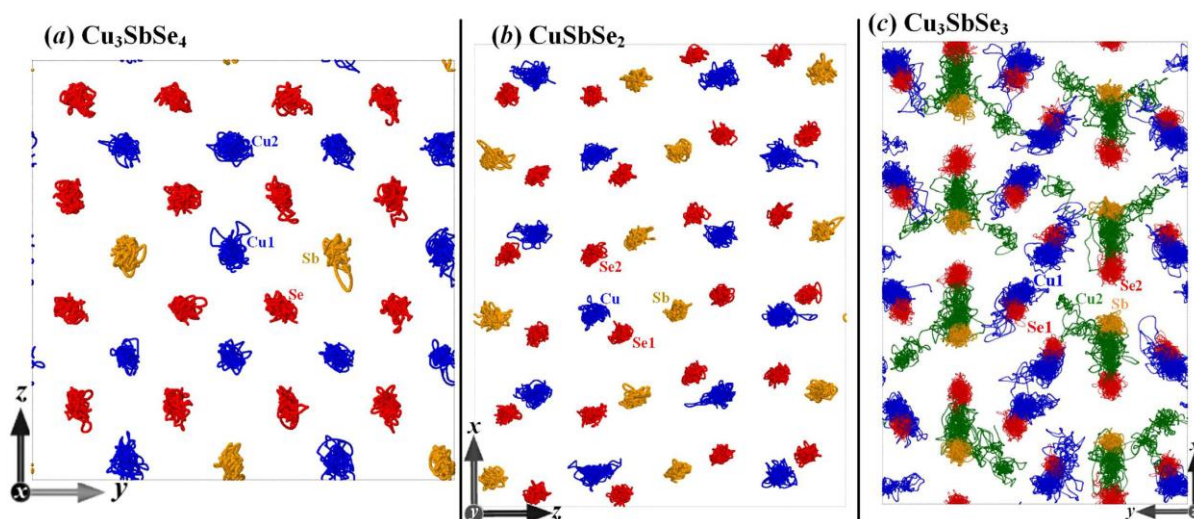


Figure 1.10 Trajectories of atoms from molecular dynamics simulations for (a) Cu_3SbSe_4 , (b) CuSbSe_2 , and (c) Cu_3SbSe_3 at 400 K. Reproduced from reference 120.

thermoelectric applications. The order/disorder transition is associated with a region of negative thermal expansion which may have important consequences for compatibility of this material in heterojunction devices.^{121,122} The fluidlike characteristic also suggests high ionic mobility through the rigid Sb/Se sublattice, implying Cu_3SbSe_3 may be of interest for ionic conduction applications.

1.6b Lone Pair Effects

Another significant difference between the Cu-Sb-Se phases is the oxidation state of antimony. The Cu_3SbSe_4 phase contains Sb^{5+} (as discussed above in section 1.5a), while antimony exists as Sb^{3+} in Cu_3SbSe_3 and CuSbSe_2 . Structurally, this is of importance due to the lone pair present with Sb^{3+} and its effect on many properties of these species.

Aside from the clearly apparent structural distortion in the SbSe_3 trigonal pyramids present in Cu_3SbSe_3 , the effect of the lone pair on Sb^{3+} is intimately related to most other material properties. A similar comparison of the Cu-Sb-Se phases proposes an explanation for the trend observed in lattice thermal conductivity. Here, a study of the high Grüneisen parameters demonstrates that they originate from the interactions of the Sb lone pair with the bonding charge present in Sb-Se bonds.^{18,118} Further, while the lone pair is indicative of the valency of antimony in these species, it also strongly impacts the thermal conductivity.¹²³

To clarify, the effective valency can be calculated from Se-Sb-Se angles,⁷⁹ which demonstrate Sb^{5+} for Cu_3SbSe_4 but effective valences of 3.36 for Cu_3SbSe_3 and 3.2 for CuSbSe_2 .⁷⁸ This is reflected in the lattice thermal conductivity (κ_{lat}) where κ_{lat} decreases in the order $\text{Cu}_3\text{SbSe}_4 > \text{CuSbSe}_2 > \text{Cu}_3\text{SbSe}_3$. It is argued that the contribution of the lone

pair to lattice anharmonicity decreases the thermal conductivity in these materials, and the higher effective valence in Cu_3SbSe_3 relative to CuSbSe_2 is indicative of softer bonding in the former (Figure 1.11). Therefore, the lattice thermal conductivity matches well with the expected trend.

1.6c Order/Disorder Transition

A third interesting aspect of Cu_3SbSe_3 is related to the fluid-like aspect of the Cu ions. Here, an order/disorder transition has been observed through changes in the unit cell lattice parameters through XRD¹²¹ and phonon frequency changes through Raman spectroscopy.¹²² The inability to fit the diffraction pattern to the room temperature structure for the material above $\sim 110^\circ\text{C}$ suggests that this transition is due to disorder in the Cu sites. This is supported by Rietveld refinement, which yields large Cu displacement parameters and low occupancies,¹²¹ akin to what would be expected for the part-liquid characteristic described earlier.^{119,120} These experimental results may be strengthened by a local structure experiment using pair distribution function and/or extended X-ray absorption fine structure analyses.

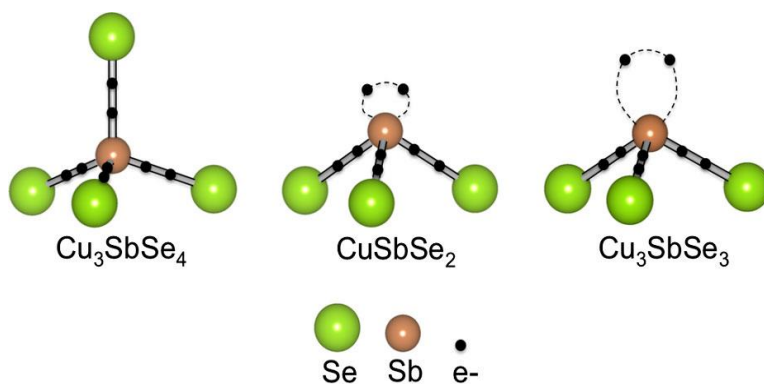


Figure 1.11 Schematic representation of the local atomic environment of Sb in Cu_3SbSe_4 , Cu_3SbSe_3 , and CuSbSe_2 . Shaded lines represent Sb-Se bonds, dashed lines illustrate the approximate morphology of the Sb lone-pair 5s electron orbital. Reproduced from reference 78.

Another interesting product of this order/disorder transition is the observation of changes in lattice parameter in this region. Aside from crystalline positions, a region of negative thermal expansion was observed.^{121,122} This may help reduce strain in heterojunctions, and in conjunction with the mechanical properties of this material,¹⁰¹ may contribute to the realization of Cu_3SbSe_3 as a desirable material for thermoelectric generation devices.

1.6d Electronic and Phonon Structure

With an understanding of the ultralow lattice thermal conductivity present in Cu_3SbSe_3 , a more thorough understanding of the electronic and vibrational structure of the material will enable additional routes to assessment and optimization of thermoelectric properties. While the lattice conductivity is anomalously low, the major contribution to κ_{tot} is still κ_{lat} ,¹¹⁷ so an understanding of the phonon modes present may help develop strategies to minimize this.

The various vibrational modes present in Cu_3SbSe_3 have been rigorously calculated and reported elsewhere.^{118,124} For the 28 atoms in the Cu_3SbSe_3 unit cell, there are 84 phonon modes.¹²⁴ Of these, three are acoustic and 81 are optical modes. Due to their low group velocities, optical phonon modes are ineffective heat transporters relative to acoustic modes and as such are typically neglected in considerations of thermal conductivity.^{18,125,126} However, these modes may still contribute to reduction of thermal conductivity by Umklapp scattering with the acoustic phonons. It was revealed that the phonon frequencies for these localized optical modes are $<250 \text{ cm}^{-1}$, such that they should all be active at temperatures $\sim 300 \text{ K}$ ¹²⁴ to contribute to phonon-phonon scattering. Experimentally, these

modes have been explored as a function of temperature using Raman spectroscopy, and this was also used to provide additional evidence of the order/disorder transition.¹²²

Cu_3SbSe_3 exhibits large Grüneisen parameters (especially relative to the other Cu-Sb-Se materials)¹¹⁸⁻¹²⁰ indicative of strong anharmonicity. Further, the average Grüneisen parameters for the acoustic modes in Cu_3SbSe_3 are comparable to similar low-thermal conductivity materials such as AgSbTe_2 ,¹²⁷ and are ascribed to the influence of the Sb^{3+} lone pair. Additionally, the transverse acoustic phonons have significantly larger Grüneisen parameters than the longitudinal acoustic mode, more effectively reducing thermal conductivity from this source. As these parameters are large due to lone pair interaction, it may be rational to tune the morphology of the crystallites to increase the density of grain boundaries normal to these interactions to increase scattering of the remaining longitudinal acoustic phonons. Similar to what has been observed in Cu_3SbS_3 ,¹²⁸⁻¹³¹ some preliminary morphological control of Cu_3SbSe_3 nanoparticles (as will be demonstrated in chapter 3) may aid in this regard.

While the lattice thermal conductivity may be decreased further, we propose that the route to optimizing ZT in Cu_3SbSe_3 should rather investigate improvements to electronic conductivity. Compared to Cu_3SbSe_4 , Cu_3SbSe_3 exhibits much lower thermal and electronic conductivities. Therefore, the poor thermoelectric performance can be attributed to poor electronic properties. The primary routes for electronic structure modification that we have detailed in section 1.5 (doping, nanoinclusions) have not yet been thoroughly investigated for Cu_3SbSe_3 . While a theoretical study of optimum dopants for this material would be ideal, it may be more complex than expected. As Cu effects were observed to contribute to the p-type character of Cu_3SbSe_4 ⁹⁸ this may be a reasonable doping site in

Cu_3SbSe_3 . Also, the enthalpies of formation of Se dopants in Cu_3SbSe_4 were found to be substantial, but the crystal structure of Cu_3SbSe_3 is significantly different such that this may be a more feasible route in the latter compound. Finally, the Sb site is the most versatile for doping in Cu_3SbSe_4 , but it may prove to be much more critical to thermoelectric function in Cu_3SbSe_3 due to the contribution of the lone pair.

Despite a lack of dopant investigation, the electronic structure of Cu_3SbSe_3 has been explored.^{117,118,124} There is still some disagreement about the band gap, with a general consensus of an indirect gap varying in magnitude from 0.24 eV to 1.32 eV along with some dispute over which states constitute the band edges.^{35,117,124,132} However, experimental measurements reveal direct band gaps of 1.31 eV¹³³ and 1.68 eV,¹³⁴ as well as an indirect gap of ~ 0.95 eV.¹³⁵ The fundamental disconnect between theory and experiment must be reconciled before calculations may be effectively used to direct advancement of the field.

Considering this disparity between theory and experiment, sound measurements must be used to guide future computation. To this end, Cu_3SbSe_3 has been experimentally studied as a thermoelectric material and its function has been characterized.^{101,117,135,136} Interestingly, while some studies reveal a nondegenerate semiconductor-like relationship between electrical conductivity and temperature,^{135,136} another demonstrates degenerate-like behavior.¹¹⁷ The argument for degenerate behavior is the possibility of Cu vacancy formation leading to a hole-doping effect due to the nature of the employed spark-plasma sintering synthesis,¹³⁵ though Liu et al.¹³⁶ also employ a SPS synthesis and found nondegenerate behavior suggesting that there may be a competing phenomenon worth

investigating in order to more completely understand electronic transport and structure in this material.

The champion preparation of phase-pure Cu_3SbSe_3 yields an electronic conductivity of $\sim 5 \Omega^{-1}\text{cm}^{-1}$ and $S \sim 400 \mu\text{VK}^{-1}$, which combine to yield $ZT = 0.25$ at $\sim 650 \text{ K}$.¹³⁵ Further, by utilizing inclusions of CuSbSe_2 and Cu_{2-x}Se , a Cu_3SbSe_3 -based material was able to bypass this performance to yield a $ZT = 0.42$ at 653 K .¹³⁶ However, the influence of the inclusion phases was not explored indicating this is an open avenue of research for further improvement in Cu_3SbSe_3 thermoelectric materials. It is also important to note that for both the phase-pure and inclusion champion samples, the trend of ZT was increasing with temperature, and is expected to continue to rise though Cu_3SbSe_3 exhibits a melting point of $\sim 730 \text{ K}$ ¹³⁵ that may limit ZT_{max} similar to the conditions observed for Cu_3SbSe_4 .

While it is difficult to refrain from comparison of Cu_3SbSe_3 and Cu_3SbSe_4 , the significantly different structures lead to a substantial difference in thermoelectric function. Both materials display a large anharmonicity that contributes to minimal thermal conductivity, but the large Grüneisen parameters and lone pair effect present in Cu_3SbSe_3 render impressive thermal barriers in this material. Though the current maximum ZT predicted for p-type Cu_3SbSe_3 is 0.7 (or 0.9 for n-type),¹²⁴ the major limitation inhibiting thermoelectric performance is the low electronic conductivity. There are a variety of ways to improve the power factor^{137,138} that may be employed here. Owing to its ultralow thermal conductivity, Cu_3SbSe_3 provides a potentially interesting thermoelectric material, though it must first be optimized electronically in order to achieve any appreciable figure of merit.

1.7 CuSbSe₂ for Thermoelectrics

A layered structure is present in several high-ZT materials such as SnSe,¹⁴ Bi₂Te₃,¹¹⁶ and BiCuSeO.¹³⁹⁻¹⁴¹ While some of these are more traditional thermoelectric systems, the discovery of a high ZT (2.6 at 923 K) in SnSe¹⁴ has suggested that the search for high efficiency thermoelectric materials may need to broaden its scope to possibly include simple structures, small unit cells, and/or low molecular weight compounds in contrast to common structure types outlined in section 1.2. In the search for new thermoelectric materials, layered compounds are desirable for their anisotropic transport properties and amenability for fabrication of high efficiency thin film thermoelectric devices.¹³

The last known member of the Cu-Sb-Se family, CuSbSe₂, is defined by a layered orthorhombic crystal structure (as is previously described in more thorough detail in section 1.4 above). While this compound is predominantly studied for its photovoltaic potential, there have still been a handful of works assessing it for thermoelectric applications. Despite some originally promising properties, CuSbSe₂ has not yet demonstrated large ZT values.

The CuSbSe₂ structure is composed of two-dimensional layers of atoms with an interlayer gap bordered by antimony. The lone pairs on Sb³⁺ are oriented to extend into the interlayer gap, and as such study of their effect on electronic properties is merited. Electronic structure of bulk and monolayer CuSbSe₂ were calculated and compared, with the largest difference being in the Seebeck coefficients.¹⁴² This suggests that the lone pair influences the thermopower, which decreases in monolayer species.

It is commonly found that CuSbSe₂ exhibits properties intermediate between the other members of the Cu-Sb-Se family. The rigid lattice is akin to the rigid bonding in Cu₃SbSe₄,¹²⁰ but the lone pair on Sb³⁺ is more similar to Cu₃SbSe₃.⁷⁸ Here, the electrostatic

repulsion of the lone pair with neighboring chalcogen ions greatly affects the anharmonicity present in CuSbSe_2 and materials with similar valency like AgSbTe_2 .^{61,78,127}

Aside from contributions to the basic understanding of thermoelectric function in CuSbSe_2 , several samples have been fabricated and characterized. Synthesized through direct fusion^{51,52,143} and mechanical alloying,¹⁴⁴ the thermoelectric properties of CuSbSe_2 are not competitive with any high-ZT materials.¹⁴⁵ Not only does CuSbSe_2 possess intermediate thermoelectric properties between Cu_3SbSe_3 and Cu_3SbSe_4 , but it also exhibits intermediate electronic properties (such as Seebeck coefficient, electrical conductivity, and partial degeneracy) relative to CuSbS_2 and CuSbTe_2 .^{51,52}

Despite the mediocre prognosis, some doping has been attempted in this compound. Both Ti^{3+} and Pb^{4+} have been used to substitute onto the Sb^{3+} site.¹⁴³ Doping with Pb^{4+} was found to have almost no effect on the overall thermoelectric efficiency, likely due to its nature as an n-type dopant in this p-type material offsetting any gains obtained through phonon scattering. In contrast, Ti-doping increased the ZT about twofold to 0.0041 at 300 K. Additional insight about electronic structure was obtained through the analysis of changes to activation energy measured in these species. Similar to the other copper selenoantimonates, the ZT was observed to increase with temperature. This result is of note as this study observed the thermoelectric behavior of Cu_3SbSe_3 at cryogenic temperatures. Increasing the temperature to 623 K for a mechanically-alloyed CuSbSe_2 sample yields a ZT of 0.25.¹⁴⁴ This work also proceeds to investigate the formation pathway of CuSbSe_2 , and determined Cu_3SbSe_4 is an intermediate phase. A 9:1 ratio of CuSbSe_2 : Cu_3SbSe_4 was then used wherein nanoinclusions of the smaller-gap Cu_3SbSe_4 serve to improve the

thermoelectric function of the material, leading to a maximum recorded ZT for a majority-CuSbSe₂ system of 0.41 at 623 K.

It is suggested that improvements to thermoelectric function in CuSbSe₂ should focus on tuning electronic properties due to the poor electronic conductivity in the material.¹⁴⁴ The optimum hole concentration for p-type CuSbSe₂ is $5 \times 10^{20} \text{ cm}^{-3}$,¹⁴² though experimentally reported values are lower than this by orders of magnitude.^{52,143,144} Therefore, as nanoinclusions of Cu₃SbSe₄¹⁴⁴ and doping with Ti¹⁴³ have improved carrier concentrations, they may be valid strategies for optimizing ZT. Despite this, the improvements to thermoelectric efficiency are minimal and not likely to support a carrier concentration sufficient to achieve appreciable thermoelectric efficiency due to the intrinsically low carrier concentration in CuSbSe₂ ($\sim 10^{17} \text{ cm}^{-3}$).¹⁴⁴ In conjunction with the intermediate properties of this material, it is our opinion that it is not likely to function as a high-efficiency thermoelectric material of interest, and that greater efficiencies may be achieved in Cu₃SbSe₃ and Cu₃SbSe₄, especially in light of the progress of these three materials (Table 1.3).

Table 1.3 Maximum ZT of Intrinsic and Engineered Cu-Sb-Se Materials by Compound.

Species	ZT	Reference
CuSbSe ₂	0.25 at 623 K	144
Cu ₃ SbSe ₃	0.25 at 650 K	135
Cu ₃ SbSe ₄	0.62 at 690 K	83
9:1 CuSbSe ₂ :Cu ₃ SbSe ₄	0.41 at 623 K	144
Cu ₃ SbSe ₃ with CuSbSe ₂ /Cu _{2-x} Se inclusions	0.42 at 653 K	136
Cu ₃ Sb _{0.88} Sn _{0.1} Bi _{0.02} Se ₄	1.26 at 673 K	73

1.8 Cu₃SbSe₄ for Photovoltaics

We now turn our focus to Cu-Sb-Se compounds and their potential in photovoltaic applications. As mentioned in section 1.3, there is an exciting push in the literature to explore new earth-abundant materials with unknown or underexplored properties. The copper antimony selenide series is a group of exciting prospects for the low material extraction costs relative to current thin film materials (Figure 1.12).¹⁴⁶

Crystallographically, Cu₃SbSe₄ adopts a famatinite structure similar to stannite Cu₂ZnSn(S,Se)₄¹⁴⁷ or zincblende of other photoabsorbers like CdTe¹⁴⁸ and GaAs.¹⁴⁹ However, despite the similarities in atomic positions and polyhedral connectivity, the electronic structure of Cu₃SbSe₄ differs greatly from that of previously mentioned photoabsorber compounds. Unfortunately, these differences are unfavorable for solar absorption in Cu₃SbSe₄, so it is worthwhile to understand the electronic structure and its contributing states.

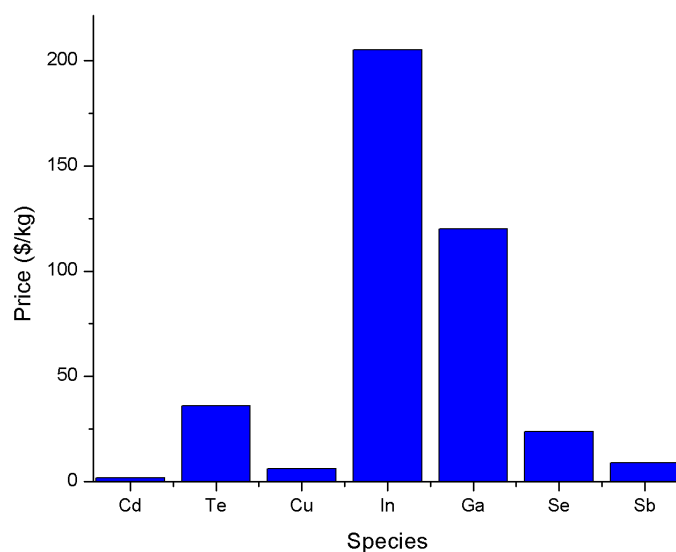


Figure 1.12 Cost of elements in commercial thin-film photovoltaic materials. Cu, Sb, and Se are inexpensive alternatives and may help lower the cost per watt in PV generation. Data obtained from the US Geological Survey.

Continuing the comparison to other diamond-like complex copper chalcogenides, the band structure of Cu(In,Ga)Se_2 is well-studied, especially as it has led this material to power conversion efficiencies up to 22.6%.²⁴ The traditional chalcopyrite CuInSe_2 has a valence band comprised of Cu-d and Se-p states with a conduction band of In-s and Se-s and Se-p states,^{150,151}. Similarly, the valence band of Cu_3SbSe_4 is made up of Cu-3d and Se-4p states.⁸¹ Also analogous to the CuInSe_2 structure, the conduction band of Cu_3SbSe_4 is constituted by Sb-5s and Se-4p states. It is important to note two differences between these two diamondlike systems. First, as is expected, the inclusion of In and Sb in these different systems will yield different band energies. Second, due to differences in stoichiometry, while both the famatinite Cu_3SbSe_4 and chalcopyrite CuInSe_2 are diamondlike structures, they involve different bonding environments as previously described. Despite similar crystal structures, the electronic nature of these materials is vastly different leading to CuInSe_2 to be studied for photovoltaic applications while Cu_3SbSe_4 has been pursued toward thermoelectrics.

Further, the electronic structure of Cu_3SbSe_4 may be interesting to supplement knowledge of Cu_3SbS_4 (another photovoltaic material),^{38,40,152,153} which crystallizes in the analogous sulfide structure. Experimentally, Cu_3SbSe_4 has been determined to be a narrow-gap semiconductor with a direct band gap of ~ 0.3 eV (Figure 1.13).^{80,89,102} It should be noted that there are a couple of reports of a significantly larger gap in this material. For instance, Ghanwat et al. have reported the synthesis of Cu_3SbSe_4 nanocrystals by microwave⁷⁵ and arrested precipitation⁷⁶ where the optical gap was reported as 1.87 eV and 1.96 eV respectively. To the contrary, measurement of room temperature properties of Cu_3SbSe_4 found the electronic gap to be 0.13 eV,¹⁰⁰ though this was attributed to the

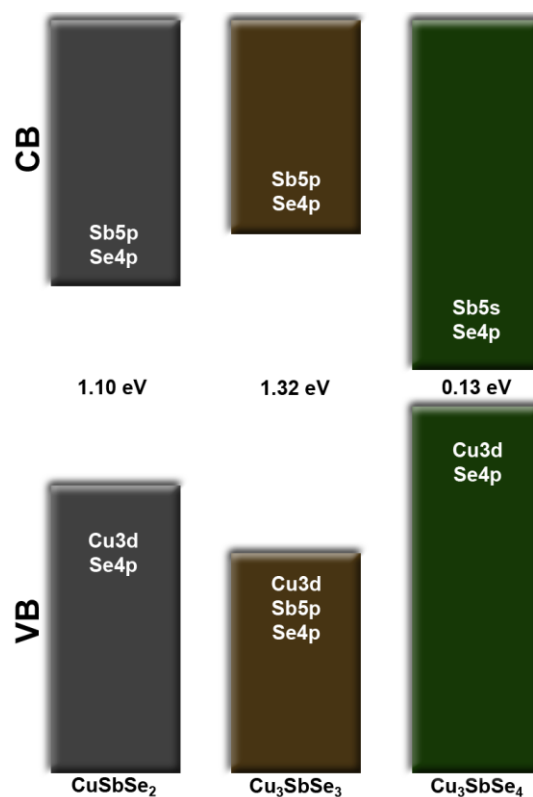


Figure 1.13 Band gaps and composition for Cu-Sb-Se species. The only valence band with antimony contributions is Cu_3SbSe_3 , while all conduction bands are similar.

activation energy instead of the band gap as it is not large enough to account for the Seebeck coefficient of this material.⁸⁰

Many authors have also probed the electronic structure of Cu_3SbSe_4 using a variety of methods. However, many calculations yield results for the electronic structure of Cu_3SbSe_4 without an energy gap separating the valence band and conduction band.^{71,154,155} Separately, use of the HSE06 hybrid functional yields results similar to experimental data, as well as GGA+U but only if an unphysically reasonable large U ($U = 15$ eV) is used.^{71,154} Calculated band gaps have ranged from metallic¹⁵⁶ to semiconducting with a magnitude of 0.20-0.4 eV.^{36,81} However, it is well known that GGA often underestimates the band gap, and this is observed for this material as well.^{71,154,156} Semiconducting behavior has,

however, been calculated for Cu_3SbSe_4 using several different levels of theory including GGA-PBE,^{73,98} HSE06^{35,71,81,154} and mBJ+U.^{36,71,155}

More thorough analysis has been provided by Do et al.,⁷¹ who performed DFT calculations to rigorously determine the electronic structure of Cu_3SbSe_4 using a variety of calculation methods. They determined that the physics of band gap formation in Cu_3SbSe_4 is subtle and relies on a “band of interest” (BOI). This BOI is a narrow band near the top of the valence band composed of Se-p, Sb-s, and Cu-d states. Therefore, the local coordination environment and oxidation state of Sb is critical to the electronic structure in this material. Further, this work reports that Cu_3SbSe_4 contains Sb^{3+} in contrast to the Sb^{5+} expected by valence counting. This is elucidated further in several XPS studies,⁷²⁻⁷⁴ where the Sb3d peaks are observed to be at lower binding energies than corresponding coordination environments for Sb^{5+} such as Sb_2Se_5 .¹⁵⁷ However, comparing XPS results of Cu_3SbSe_3 and Cu_3SbSe_4 suggests that Sb exists in the 5+ state in Cu_3SbSe_4 as the binding energy is significantly higher in Cu_3SbSe_4 than Cu_3SbSe_3 , and in Cu_3SbSe_4 there is only one Cu and one Se binding environment observed, while one of these sites must be aliovalent in order to contain Sb^{3+} . Further corroboration can be found in results from XANES⁶¹ and hole concentration arguments.⁸⁰ Therefore, in Cu_3SbSe_4 only one oxidation state of antimony, Sb^{5+} , exists⁷⁸ though its binding energy may be lower than expected.

Overall, while Cu_3SbSe_4 is a narrow-gap nondegenerate semiconductor with subtle electronic structure, HSE06 and mBJ+U appear reproduce experimental results. Knowledge of the electronic structure for this material may contribute to our understanding or optimization of other systems, but Cu_3SbSe_4 does not merit further investigation for

photovoltaic applications due to its inappropriate band gap magnitude for efficient solar absorption.

1.9 Cu₃SbSe₃ for Photovoltaics

Despite the main body of literature investigating Cu₃SbSe₃ as a thermoelectric due to its minimal lattice conductivity, this compound has also demonstrated potential as a feasible solar photovoltaic absorber material. With a calculated SLME of 17.7%,³⁵ Cu₃SbSe₃ could surpass the current benchmark power conversion efficiency for earth-abundant materials of 12.6% achieved by CZTSSe.³⁰ However, this SLME was calculated using G₀W₀@HSE06, which may not yield accurate results for this class of material.^{155,158} Instead, mBJ+U results reveal an indirect band gap as low as $E_g^i = 0.88$ eV for Cu₃SbSe₃.^{36,159} This is significantly lower than the 1.32 eV indirect gap determined by G₀W₀@HSE06,³⁵ but it does predict a good band alignment with CdS, proposing that well-optimized CIGS and CZTS systems may easily translate to device architectures for Cu₃SbSe₃.

Aside from the band gap magnitude, study of the electronic structure in this material is critical to its function as a photovoltaic component. Similar to other copper chalcogenidoantimonates, Cu₃SbSe₃ has a valence band composed of Cu and Se states and a conduction band of Sb and Se states.¹³² However, unlike the other species in this system, Cu₃SbSe₃ also has contributions from Sb p states to its valence band. Further, there is some Sb s and Se p mixing which fills an antibonding state at the top of the valence band to give rise to the lone pair on antimony. Different Cu₃MCh₃ (M = Sb, Bi; Ch = S, Se) species were observed, and it was determined that the lone pair effects are diminished in Bi- and

Se-containing analogues relative to Sb- and S-containing materials of this type.^{160,161} Similarly to the other computational work that studied Cu_3SbSe_3 using HSE06,³⁵ Cu_3SbSe_3 was revealed to possess a large bandgap with the smallest transition being indirect in nature with larger direct and optical gaps. This may still be acceptable, as an optical gap higher than the lowest energy transition can still yield a fruitful photovoltaic absorber material, so long as the difference in energy is small.³⁴

While theory determined Cu_3BiSe_3 has a higher potential to be used as a photovoltaic absorber than Cu_3SbSe_3 , the latter compound should be investigated, especially for full defect analysis and valence band alignment.¹³² Although the groundwork for this system has been underway since it was first studied for photovoltaics in 2003,¹³⁴ experiments are limited.

Unfortunately, the limited works that study Cu_3SbSe_3 for photovoltaics have yet to yield a phase-pure bulk sample (though these samples have been produced and studied for crystallographic and thermoelectric purposes). However, a few samples of pure phase nanocrystalline Cu_3SbSe_3 has been synthesized via a hot injection route.^{133,162} Despite this, the reported properties of all Cu_3SbSe_3 samples suffer from either the possibility of impurities affecting absorption properties or a high density of grain boundaries adversely affecting electronic transport. Apart from the previously mentioned electrodeposition/chemical bath¹³⁴ and hot injection¹³³ routes, Cu_3SbSe_3 has been synthesized as a phase-pure bulk sample through traditional solid state methods^{50,55,62,117,121,135} indicating that a fundamental study of photovoltaic properties present in a phase-pure sample may be possible by milling an as-synthesized sample to fabricate a thin film. Further insight into impurity formation can be obtained through

analysis of the growth of these crystals. Interestingly, solid-state,⁶⁶ chalcogenization,¹⁶³ and electrodeposition/chemical bath¹³⁴ techniques all indicate complex crystalline formation pathways which are contrasted by the one-step growth mechanism observed for the hot injection route.¹³³ Despite the conversion of Cu_3SbSe_3 to Cu_3SbSe_4 at longer times through this method, it suggests that hot injection is a promising platform for phase-pure synthesis, and further this technique is amenable for facile thin-film fabrication through drop-casting, dip-coating, and spin-coating.¹⁶⁴⁻¹⁶⁷

Indeed, using the hot-injection route, preliminary optoelectronic properties of Cu_3SbSe_3 nanocrystals were reported.¹³³ Exhibiting a direct bandgap of 1.31 eV, the p-type Cu_3SbSe_3 thin film deposited on ITO yields a current density of $J_{\text{SC}} = 0.22 \text{ mAcm}^{-2}$. This is accompanied by an incident photon-to-current efficiency (IPCE) of 10-35% for wavelengths ranging from 400-980 nm, indicating that Cu_3SbSe_3 is a capable photoabsorber, and photogenerated holes can be extracted under these unoptimized conditions. Surprisingly, these IPCE values are greater than those of the dichalcogenide systems CuSbS_2 ¹⁶⁸ and CuSbSe_2 ,¹⁶⁹ which have projected higher maximum theoretical power conversion efficiencies.³⁵ This may suggest there are competing phenomena present in these materials, or perhaps current DFT models have left something unaccounted for Cu_3SbSe_3 .

While no full photovoltaic cell has been reported for Cu_3SbSe_3 , a device was structured using a substituted sulfide.¹⁶³ Starting with cubic Cu_3SbS_3 , Se was substituted onto S sites to yield $\text{Cu}_3\text{Sb}(\text{Se}_x\text{S}_{1-x})_3$ ($0 \leq x \leq 0.49$). The substitution was noted by the changes in lattice parameters as well as the decrease of bandgap with increasing Se content. However, though multiple polymorphs of Cu_3SbS_3 exist, a cubic phase is unknown.^{55,56}

Instead, we propose that this may be a sulfur-deficient $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, as the X-ray diffraction pattern mimics that of tetrahedrite structures.^{57,170} If this work indeed studies tetrahedrite, it may provide exciting possibilities for the formation of the mixed chalcogenide, as the reported stoichiometry is richer in Se than the reported solubility limit of Lu et al.¹⁷¹ Confusion between these phases may be due to the extensive composition field for tetrahedrite,^{172,173} though thorough crystallography of the structures of the Cu-Sb-S system can be found for clarification.^{56,174-176}

Regardless of the structure, the substitution of selenium for sulfur is still of interest with this stoichiometry in regard to solar absorbing materials. The bandgap of these materials decreases from 1.84 eV for Cu_3SbS_3 to 1.38 eV for the maximum selenium inclusion, with a projected bandgap of 0.71 eV for the pure selenide. However, this phase has not been obtained experimentally, consistent with the lack of observation of any cubic polymorphs of Cu_3SbSe_3 . In this system, open circuit potentials and short circuit current densities of 1-3.5 mV and 1.0-1.6 mAcm^{-2} were reported for the material with the ratio $\text{Se}/(\text{S}+\text{Se}) = 0.08$. While this current density is higher than that of the nanocrystalline Cu_3SbSe_3 ,¹³³ the low open circuit potential and difficulty of synthesis for the pure selenide render this a relatively unattractive candidate for use in solar cells.

Despite the poor photovoltaic characteristics of this mixed chalcogenide phase, the orthorhombic pure selenide phase Cu_3SbSe_3 merits further investigation. The first step to validate the potential of this phase as a photovoltaic material involves ensuring the agreement of theory and experiment. The two DFT screening studies cited here find very different band gaps for Cu_3SbSe_3 by $\text{G}_0\text{W}_0@HSE06$ ³⁵ and $\text{mBJ}+\text{U}$,³⁶ but to date it is uncertain which more accurately models Cu_3SbSe_3 and similar materials. This is due to the

lack of existing reproducible experimental evidence. Experimentally-determined direct band gaps range from 1.31 eV¹³³ to 1.68 eV,¹³⁴ while an indirect gap has been measured at 0.95 eV.^{68,135} Unfortunately, the electronic measurements obtained experimentally for Cu₃SbSe₃ often reflect the properties of a mixture of phases, and while Cu₃SbSe₃ is the major phase the optical data may be affected by the presence of CuSbSe₂ and/or Cu₂Se.

Experimentally, a phase pure material must be synthesized and analyzed for its optoelectronic properties. Impurities may contribute to absorbance or electronic transport, and therefore may convolute understanding of the properties of Cu₃SbSe₃. This should be fairly straightforward as there are multiple methods of synthesizing phase pure Cu₃SbSe₃. Of these, hot injection is a promising technique, though the products are nanocrystalline and as such may require annealing or alternative techniques to grow the grains in order to avoid recombination at grain boundaries.¹⁷⁷⁻¹⁸¹ Clearly, there remains much to be optimized synthetically before considering developing and improving device architectures. However, the similarities in properties of Cu₃SbSe₃ with known photovoltaic systems such as CZTS and CIGS may allow for application of the already established knowledge base to transfer from these fields. This would decrease the barriers to exploration of Cu₃SbSe₃ as a promising (albeit often overlooked) photovoltaic material.

1.10 CuSbSe₂

The final material in the Cu-Sb-Se system, CuSbSe₂, is the most thoroughly explored for photovoltaics, and a brief summary of progress with this material and CuSbS₂ has been reported by Ganose et al.¹⁸² Owing to its promising absorption properties, CuSbSe₂ is projected to be comparable to, or even surpass CuInSe₂ as a photovoltaic.³⁵ As we have

detailed earlier, CuSbSe₂ possesses a layered orthorhombic structure of corner-sharing polyhedra. Interestingly, the lone pairs of Sb³⁺ extend into the interlayer spaces and may provide interesting properties.^{44,142}

1.10a Thin Films

In our previous discussion of thermoelectric CuSbSe₂ (Section 1.7), we detailed several syntheses of bulk CuSbSe₂. However, in contrary to these previous works, thin films are desired for generation II photovoltaic materials.^{183,184} Synthesis of thin-film CuSbSe₂ has been achieved through electrodeposition,^{169,185} annealing in a chalcogen environment,¹⁸⁶ mechanical alloying followed by e-beam evaporation,¹⁸⁷ combinatorial sputtering,^{188,189} and hydrazine^{190,191} routes.

All optoelectronic thin film reports of CuSbSe₂ conclude that its properties are amenable to photovoltaic function. These typically include direct band gaps of ~1.10 eV and optical absorption coefficients of $\alpha > 7 \times 10^4 \text{ cm}^{-1}$,¹⁸⁵ though optical absorption as high as $\alpha > 10^6 \text{ cm}^{-1}$ has been reported.¹⁸⁷ Similarly, electronic measurements demonstrate a p-type conductivity with typical hole concentrations of 10^{16} - 10^{17} cm^{-3} ,^{143,144,185,188,189,191} the lowest carrier concentration in the Cu-Sb-Se system. Further, photoactivity measurements on thin films of CuSbSe₂ reveal efficient photogeneration and subsequent carrier extraction as observed through photocurrent-potential response.¹⁸⁵ Similar to what has been observed in other copper chalcogenide systems,^{192,193} the stoichiometry of CuSbSe₂ is intimately related to its photovoltaic properties. Through IPCE measurements, it was determined that CuSbSe₂ displays more advantageous photovoltaic properties when composed of Cu-poor stoichiometries.¹⁶⁹

Aside from bulk samples, thin films may also be fabricated from nanocrystalline species. To this end, CuSbSe₂ has been synthesized via hot injection^{162,194,195} and heat-up¹⁹⁶ methods. While some of these works utilize more traditional nanocrystalline synthetic conditions using oleylamine,^{194,196} considerations surrounding this solvent/surfactant have been detailed further elsewhere and as such will not be covered in depth here.¹⁹⁷ However, citing issues with oleylamine reduction of antimony,¹⁹⁸ Hsiang et al. report a hot injection route to phase-pure CuSbSe₂ involving triethylene glycol with triethylenetetramine as a coreducing agent.¹⁹⁵ In this method, formation of CuSbSe₂ proceeds through an intermediate, with formation of Cu₃SbSe₄ and Sb₂Se₃ eventually leading to CuSbSe₂. Interestingly, this proposed reaction contains excess selenium that is not accounted for by the products, though it may wash away during particle workup. This is similar to the growth mechanism rationalized for CuSbS₂ grown through a hot injection technique.¹⁹⁹ The limiting factor in growth of the CuSbSe₂ phase is attributed to reduction of Cu²⁺ to Cu⁺ by triethylenetetramine. Further, if Cu²⁺ converts to Cu⁺ via reduction by triethylenetetramine, this then suggests that the rate limiting step in the formation of CuSbSe₂ is the formation of Cu₃SbSe₄ as the latter compound already contains a Cu⁺ species.

The morphology of these nanocrystals reflects the layered crystal structure of CuSbSe₂. Nanocrystalline materials synthesized through the oleylamine routes exhibit a plank-like or belt-like morphology.^{194,196} This is also present in larger grain samples, though here organic amines are also credited as structure-directing agents⁴⁶ as has been shown for similar amine-based organic-inorganic copper chalcogenidoantimonates.²⁰⁰⁻²⁰² Further, this morphology draws comparisons to analogous sulfides that exhibit anisotropic

brick-like structures.^{168,194,203} In fact, several works have gone so far as to use solid solutions of the sulfur-selenide materials in order to tune the properties in this system.

1.10b Mixed Chalcogenide CuSb(S,Se)₂

The mixed chalcogenide CuSb(S_xSe_{1-x})₂ has been achieved through a variety of syntheses and often exhibit shape anisotropy (Figure 1.14). It is important to note here that thiols are common in solution-phase synthesis of similar materials,²⁰⁴⁻²⁰⁷ though for a mixed-chalcogenide material it may be of concern whether both elements are present in the lattice or if one species is solely bound to the surface. Using XPS, it was shown that sulfur does fully incorporate into the lattice.¹⁹⁶ Further, in these solution-phase routes the composition of the products could be controlled by the concentration of diphenyldisulfide.¹⁹⁴ These materials exhibit an indirect band gap that is slightly smaller than the direct gap, though both follow Vegard's law with incorporation of sulfur.²⁰⁸ Therefore, the direct band gaps are tunable from $E_g^d = 1.08$ eV for the pure selenide to $E_g^d = 1.45$ eV^{208,209} for CuSbS₂. By extension, as the composition changes, so does the band

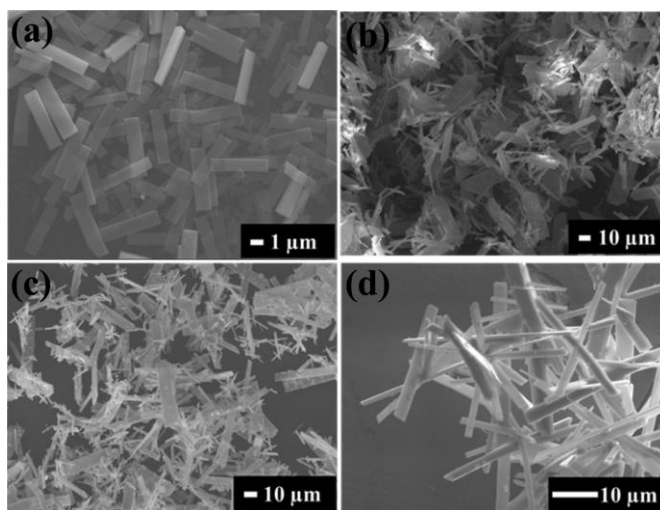


Figure 1.14 Scanning electron microscope images of CuSbSe_xS_{2-x}, exhibiting anisotropic morphology. (a) $x = 0$, (b) $x = 1$, (c) $x = 1.5$, and (d) $x = 2$. Adapted from reference 194.

structure. The valence band maximum becomes deeper in energy as the concentration of sulfur increases ranging from -5.15 eV for CuSbSe₂ to -5.45 eV for CuSbS₂. Simultaneously, the conduction band minimum slightly increases from -4.07 eV for CuSbSe₂ to -4.00 eV for CuSbS₂.²⁰⁹ These observations demonstrate a similarity to the band positions for CuInSe₂,^{210,211} suggesting that the success of the CIGS system may prove fruitful for CuSbSe₂ as well. However, as work with CuSbS₂ demonstrates that the electronic structures of these two systems are not as similar as they may initially seem,²¹² it may instead be more prudent to utilize the knowledge gained from studies of CuSbS₂ devices²¹³⁻²¹⁸ and their defect characteristics²¹⁹ to inspire future direction for CuSbSe₂. Despite the similar structures, these different materials therefore require a more thorough understanding of electronic properties before full photovoltaic cells may be further optimized.

Several theory studies have been performed on CuSbSe₂ and its related chalcogenides (CuSbS₂, CuBiS₂, and CuBiSe₂) with respect to their application in solar photovoltaics. Electronic structure calculations using HSE06 reveal an indirect band gap larger than those experimentally reported with values ranging from $0.93 \text{ eV}^{48} < E_g^i < 1.36 \text{ eV}^{95}$. Though the identities of the VBM and CBM vary in these calculations, they all determine that a direct gap exists only slightly higher in energy with $1.04 \text{ eV}^{48} < E_g^d < 1.41 \text{ eV}^{95}$. While these calculations overestimate the band gap determined experimentally, it is important to note that though experimental band gaps of CuSbSe₂ have been determined primarily through optical absorption, one example uses photoemission yield spectroscopy.²⁰⁹ Therefore, these results combine to demonstrate that regardless of

disagreements between theory and experiment, all studies have concluded that a band gap exists in CuSbSe₂ of an appropriate magnitude for solar absorption.

1.10c Crystallographic and Electronic Structure

The crystal structure of CuSbSe₂ was also worthy of consideration, and has been elucidated by theory.⁴⁸ While many common copper chalcogenide photovoltaic materials such as CuInSe₂ adopt zincblende-based structures, CuSbSe₂ crystallizes in the orthorhombic chalcostibite structure which is a wurtzite derivative. It has been noted that the nature of chalcostibite as a layered structure may be detrimental to function as a photovoltaic material,²²⁰ similar to the anisotropic electronic properties observed in layered SnS.^{221,222} The origin of the chalcostibite CuSbSe₂ phase (enthalpy of formation $\Delta H^0 = -262.4$ kJ/mol) was determined to be the lone pair on antimony which disfavors formation of the as-yet unknown chalcopyrite CuSbSe₂ phase ($\Delta H^0 = -200.6$ kJ/mol).⁴⁸

Aside from structural considerations, the lone pair may also contribute to electronic properties. One study observed a slight contribution of Sb5s states to the valence band.²²⁰ They further found weaker carrier mobility in CuBiSe₂ than CuSbSe₂, suggesting that the lone pair may affect transport properties adversely due to the stronger influence of the lone pair on properties of the antimony species relative to those of the bismuth species.

Apart from electronic structure, optical absorption is also critical for success of a photovoltaic absorber material. Optical absorption coefficients were calculated for CuSbSe₂ and compared to those of CuInSe₂. All studies determined a high absorption coefficient for CuSbSe₂, with results yielding absorption either comparable to⁴⁸ or greater than CuInSe₂.⁹⁵

While CuSbSe₂ is not a chalcopyrite-type absorber material, these calculations reveal several properties that make it interesting for investigation with respect to earth-abundant photovoltaics. The antimony lone pair affects both crystallographic and electronic structure, but may negatively affect carrier transport. The chalcostibite structure is also layered, which may detract from photovoltaic function. Despite this, CuSbSe₂ possesses a direct band gap that, while larger than the fundamental gap, is acceptable for solar spectrum absorption. Finally, the localization of the Sb5p orbitals contributes to strong optical absorption properties. These properties lead to some debate about whether CuSbSe₂ is worth investigating further with some authors concluding that it has promising photovoltaic properties^{48,95} and others that its detriments are too significant.²²⁰ In spite of these prognoses, full devices of CuSbSe₂ have been fabricated which provide further insight to photovoltaic function and carrier transport within this material.

1.10d Full Photovoltaic Devices

The first published example of a full photovoltaic cell using CuSbSe₂ as the absorber material was reported in 2015.¹⁸⁸ Here, CuSbSe₂ was sputtered from binary Cu₂Se and Sb₂Se₃ targets to yield a thin film with irregular grains larger than 1 μm . Further, a summary of deposition conditions as a function of temperature and pressure of Sb₂Se₃ was reported to achieve phase-pure CuSbSe₂. Similar to sputtering of oxides,^{223,224} the partial pressure of Sb₂Se₃ was found to affect not only phase formation, but also defect density and carrier concentration.¹⁸⁹

Devices were fabricated using the architecture ZnO/CdS/CuSbSe₂/Mo, and the average values for the cells are as follows: $V_{oc} = 346 \text{ mV}$, $J_{sc} = 20.5 \text{ mA/cm}^2$, $FF = 43.9$, η

= 3.12%.¹⁸⁸ While the fill factor is low, it stands to reason that this is acceptable for an initial device study, and that optimization may lead to a higher value. Interestingly, the low V_{oc} is tentatively attributed to device architecture issues including the possibility of a cliff-like band offset at the heterojunction, which contrasts the low V_{oc} in multinary absorbers commonly associated with cation disorder. However, it should be mentioned that photoemission yield spectroscopy results published elsewhere²⁰⁹ yield different results for the band offset. Finally, there is room for improvement in the J_{sc} , which is limited by the thickness of the films.

It may be worthwhile to place this power conversion efficiency into context. As seen in Figure 1.1, the progress of CuSbSe₂ has recently risen steeply, and is poised to reach appreciable efficiencies in the near future. The rapid improvement of CuSbSe₂ cell efficiencies is promising, though for full optimization it is necessary to further investigate how these cells operate.

To better understand device function, a bevy of other measurements were made in this system.^{188,189} Optically, CuSbSe₂ possesses a close-to-ideal direct band gap $E_g^d = 1.1$ eV with a high optical absorption coefficient $\alpha = 7 \times 10^4 \text{ cm}^{-1}$ at 900 nm. Despite the beneficial optical properties, electronic characterization demonstrates possible underlying issues. Small minority carrier diffusion lengths (80 nm)¹⁸⁹ suggest significant recombination losses, and a high hole concentration ($2 \times 10^{17} \text{ cm}^{-3}$) contributes to a small depletion width (135 nm), though in these cells 50% of the photons are absorbed in the space charge region.

Transient optical pump THz probe reflection spectroscopy was also used to analyze photoexcited properties in CuSbSe₂.¹⁸⁹ Photoexcited charge carriers demonstrate a lifetime

of 0.2 ns, which is much larger than that of comparable 3D structures suggesting 2D layered materials may be beneficial in this regard over more traditional absorbers. Along with the longer carrier lifetimes, carrier mobility in CuSbSe₂ was measured to be $\sim 12 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Despite these properties, the diffusion length in CuSbSe₂ is 80 nm which is considerably low when compared to the μm diffusion lengths in CIGS.²²⁵⁻²²⁷ This short carrier diffusion length could be due to a short lifetime (from a more defective material) and lower mobility due to higher electron effective mass ($m_e^* = 2.5 m_0$ for CuSbSe₂). However, these two specific properties are of interest in this system.

First, while CuSbSe₂ may possess a larger concentration of defects, they are most likely V_{Cu} (acceptor) and Cu_i (donor) defects,^{189,190} which differ from those of the more well-studied systems CIGS²²⁸ and CZTS.^{32,229} In order to avoid formation of both V_{Cu} and Cu_i (which would compensate each other and negate doping effects), it is therefore desirable to grow CuSbSe₂ under Se-rich conditions. Further, the only defects with appreciable populations are shallow defects, supporting CuSbSe₂ as a good solar cell absorber material.¹⁹⁰

The other property of interest, the higher effective mass, may decrease carrier mobility but it also contributes to the large absorption coefficient. Therefore, the balance of absorption with transport results in a drift-enhanced solar cell operation as opposed to the diffusion-dominated operation typical for CIGS.

Using this analysis, another cell was fabricated with the same architecture. By adjusting the composition of the materials, a champion film was produced with $J_{\text{SC}} = 26 \text{ mAcm}^{-2}$, $V_{\text{OC}} = 336 \text{ mV}$, $\text{FF} = 53\%$, and an overall $\eta = 4.7\%$.¹⁸⁹ This is the largest power conversion efficiency to date reported for CuSbSe₂ (photovoltaic cell comparisons for

CuSbSe₂ may be found in Table 1.4). Interestingly, V_{OC} values were constant for Cu-poor compositions, but fell to zero for Cu-rich compositions. This suggests Sb₂Se₃ impurities do not adversely affect open circuit potential, though the high-carrier concentration Cu₃SbSe₃ impurities render the cell less effective. Short-circuit current density plots show similar behavior, though they also exhibit a spike in J_{SC} at the stoichiometric composition which is attributed to lower absorption of red photons in the Cu-rich species as well as a smaller depletion region.

This trade-off between V_{OC} and J_{SC} may limit maximum power conversion efficiencies. To address this, Na incorporation in these devices was attempted, as this has been used to affect electronic structure and improve PV performance in other Cu-chalcogenide solar cells.²³⁰⁻²³² While Na incorporation does increase the V_{OC} , simultaneously the J_{SC} decreases rendering this method ineffective at increasing η and decoupling the trade-off between V_{OC} and J_{SC} . However, it should be mentioned that the comparable CIGS experiment in this study only exhibited a PCE of 7.5%, suggesting that there may be significant improvement in CuSbSe₂ devices by optimization. Suggested routes include annealing in a Se environment, or by optimizing the band offset of the

Table 1.4 Electronic properties of CuSbSe₂ thin films.

Synthesis	E_g (eV)	α (cm ⁻¹)	Hole concentration (cm ⁻³)	V_{OC} (mV)	J_{SC} (mAcm ⁻²)	Fill Factor (%)	η_{max} (%)	Reference
Chalcogenization	~1.2							186
Electrodeposition	1.09	7 x 10 ⁴						169
Electrodeposition	1.10	7 x 10 ⁴	5.8 x 10 ¹⁷					185
E-beam evaporation	~1.18	>10 ⁵						187
Combinatorial sputtering	1.1	7x10 ⁴	2x10 ¹⁷	346	20.5	43.9	3.5	188
Combinatorial sputtering			10 ¹⁶ -10 ¹⁸	336	26	53	4.7	189
Hydrazine processing	1.04	10 ⁴ -10 ⁵	9.76x10 ¹⁷	274	11.84	40.51	1.32	190
Hydrazine processing			10 ¹⁷	360	20.52	36.68	2.70	191

heterojunction. Ultimately the drift-based device function in these cells leads to the trade-off between V_{OC} and J_{SC} , which must be bypassed in order to improve the overall power conversion efficiency for this material.

Reported at the same time as the first sputtering cell, a hydrazine-based approach was taken to develop a full cell with $CuSbSe_2$ as the absorber layer.¹⁹⁰ This route was chosen for its ability to manufacture a variety of high efficiency CZTSSe cells.^{30,233,234} The $CuSbSe_2$ product formed according to the proposed reaction $2[Cu_6S_4]^{2-} + 3[Sb_4Se_7]^{2-} + 10[N_2H_5]^+ + 3Se \rightarrow 12CuSbSe_2 + 10N_2H_4 + 5H_2S + 3S$, and by annealing the deposited material films 700 nm thick (with a grain size of 600 nm) were formed. These films exhibit optoelectronic properties similar to those reported in the other full cell absorber layers,^{188,189} though with a slightly higher hole concentration and mobility. These properties support previous experimental results demonstrating the efficiency of $CuSbSe_2$ to absorb light, with 99% of incident solar photons absorbed by a $CuSbSe_2$ layer 500 nm thick.

Using this hydrazine route, a photovoltaic cell was fabricated using the architecture FTO/ $CuSbSe_2$ /CdS/ZnO/ITO/Al (Figure 1.15).¹⁹⁰ The champion cell exhibits $J_{SC} = 11.84 \text{ mAcm}^{-2}$, $V_{OC} = 274 \text{ mV}$, $FF = 40.51\%$ which combine to yield $\eta = 1.32\%$. Losses in

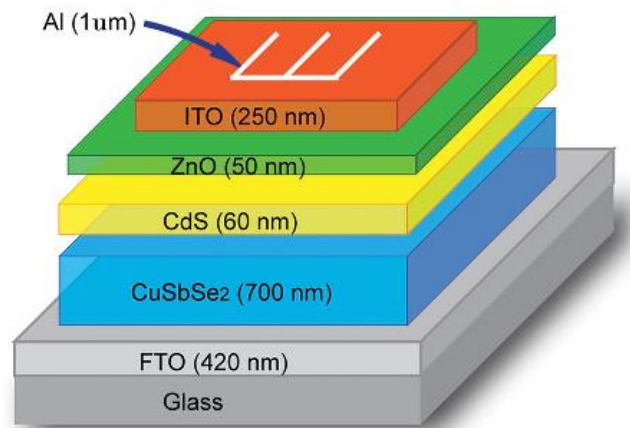


Figure 1.15 Depiction of $CuSbSe_2$ PV cell. Adapted from reference 190.

efficiency are again attributed to limitation with band alignment, defect passivation, and film quality.

Despite low power conversion efficiencies, CuSbSe_2 possesses another handle that differentiates it from traditional copper chalcogenides like CdTe and CIGS . The layered 2D structure of CuSbSe_2 suggests that there is a preferred orientation that may be exploited to increase the cell efficiency. By orienting the layers of CuSbSe_2 perpendicular to the substrate, carrier transport through the film may be facilitated and render grain boundaries benign.¹⁹¹ Using a small amount of sulfur, the precursor solution is termed “Se-poor” in order to avoid $\text{Cu}_3\text{Sb}(\text{S},\text{Se})_4$ impurity phases with a small band gap and high hole concentration that may shunt the subsequent device.

Deposited films were annealed at varying temperatures to understand phase formation. At temperatures below 380°C , Cu_3SbSe_3 forms before CuSbSe_2 . The two samples annealed at 380°C and 400°C both exhibited phase pure CuSbSe_2 , while all samples annealed at higher temperatures (up to 520°C) exhibit peaks indexed to Cu_3SbSe_3 , demonstrating the decomposition of CuSbSe_2 to Cu_3SbSe_3 at higher temperatures. While the phase pure CuSbSe_2 films exhibit electronic properties similar to those previously reported,¹⁸⁸⁻¹⁹⁰ the films deposited below 380°C or above 400°C exhibit properties indicative of the presence of Cu_3SbSe_3 .

Aside from phase formation, temperature was determined to have profound impacts on crystallographic orientation. At temperatures above 400°C , CuSbSe_2 grows with the (001) plane parallel to the substrate. This is undesirable as it necessitates charge transport across layers. However, when grown at 380°C the crystallographic orientation of CuSbSe_2 is not parallel to the substrate. Therefore, a device with this orientation was fabricated with

the architecture Mo/CuSbSe₂/CdS/IZO/AZO and produced $J_{SC} = 20.52 \text{ mAcm}^{-2}$, $V_{OC} = 360 \text{ mV}$, and $FF = 36.68\%$ which result in $\eta = 2.70\%$. While the efficiency of this cell was limited due to inefficient band alignment with CdS and poor quality IZO/AZO, the V_{OC} and J_{SC} were higher relative to the previous film¹⁹⁰ indicating that the orientation of CuSbSe₂ grains may be used to improve charge transport within the material, and can serve as a method for improving efficiency using this layered-structure material in future devices. With respect to the poor band alignment, initial work has been undertaken to explore alternative buffer layer materials for similar high-conduction band minimum absorber layers.²³⁵

Despite the power conversion efficiency in CuSbSe₂-containing devices limited to <5%, the material provides some excellent prospects for moving forward. The prototype devices already demonstrate open circuit potentials approaching those of some current materials like CZTS (though we acknowledge the V_{OC} of CZTS are typically lower than other high-efficiency photovoltaic absorber materials).²³⁶ This, in conjunction with fill factor and J_{SC} values show that CuSbSe₂ has the potential to be used in solar cell applications.

1.10e Impact on Search for Novel Photovoltaic Materials

Aside from the device efficiency, CuSbSe₂ is an interesting material for photovoltaics. The layered structure of CuSbSe₂ provides a handle for minimizing recombination sites through saturated coordination at the surface, and the orientation of the layered structure can be used to tune carrier transport through a device. This stands in stark contrast to most high-efficiency photovoltaic absorber materials that exhibit a 3-D

structure, including Si, CdTe, CIGS, and CZTS. The success of solar cell devices employing chalcostibite CuSbSe₂ demonstrate a promising avenue for alternative materials that are not only earth-abundant, but of a noncanonical structure type. This allows us to broaden our search criteria for feasible photovoltaic materials.

The inclusion of the lone pair on Sb³⁺ provides interesting electronic and structural properties for CuSbSe₂. As CuSbSe₂ contains the same oxidation states as CuInSe₂, these two systems are often compared. Differences in electronic contributions from Sb³⁺ and In³⁺ are manifest not only in CuSbSe₂ favoring the chalcostibite structure over chalcopyrite, but may also contribute to Sb orbitals and the high optical absorption coefficient. Therefore, influence of lone pairs may be another characteristic to include in the search for new solar absorber materials.

These implications for broadening the search for feasible solar absorber phases are due to the potential that CuSbSe₂ has already achieved. Modest efficiencies to date can be optimized through appropriate band alignment and device structuring, though efficiencies are limited by the trade-off of V_{OC} and J_{SC} in the drift-enhanced operation of CuSbSe₂ devices. Primarily, the only heterojunction experimentally explored as yet has been CdS, which is notably an inefficient junction.^{188,189,191} Reported band positions for CuSbSe₂^{36,190,209} may be used to identify an appropriate n-type companion so that additional work can be performed to optimize film thickness, crystallographic orientation, and stoichiometric composition. The achievement of $\eta = 4.7\%$ is a promising result for a prototypical device, and the foundations of research have been established demonstrating CuSbSe₂ as a promising photovoltaic material that merits a great deal of study for alternative solar absorbers.

1.11 Other Applications

Aside from thermoelectrics and photovoltaics, Cu-Sb-Se have been suggested for other applications based on their earth-abundant nature and desirable electronic structure. These include improvements to traditional solid state synthesis, optoelectronics, and energy storage/conversion. In this section, we will detail some of the work that has been pursued with Cu-Sb-Se materials to these ends.

1.11a Promotion of CIGS Formation

Antimony has been used to promote phase formation in CuInSe_2 .^{237,238} It was determined that Sb could be used to improve film morphology and grain size. By using stoichiometric Cu_2Se , In_2Se_3 , and Sb_2Se_3 , Yang et al. demonstrated that Sb can be used to achieve CuInSe_2 with large grain sizes and acceptable electronic properties.²³⁹ Owing to their lower melting points, formation of CuSbSe_2 and/or Cu_3SbSe_4 would be favorable en route to synthesis of CuInSe_2 . Further, Cu_3SbSe_4 possesses a crystal structure similar to that of the chalcopyrite CuInSe_2 while CuSbSe_2 exhibits electronic structure and conductivity similar to that of CuInSe_2 suggesting these may not detract significantly from properties of the final CuInSe_2 product. By doping up to 1 mol % Sb, small changes were observed in optical absorption profiles, electronic conductivity, and band gap. However, any detriments to $\text{CuIn}_{1-x}\text{Sb}_x\text{Se}_2$ properties are offset by the driving force of the Sb to reduce the temperature needed to synthesize CuInSe_2 while achieving large grains due to enhanced atomic diffusion through the Sb-containing flux.

An alternative hypothesis for the Sb-promoted formation of CuInSe_2 was proposed wherein inclusion of Sb leads to generation of Cu_3SbSe_3 which acts as a synthetic flux.²⁴⁰

Utilizing a solution-based route, it has previously been shown that Cu-Se binary phases form kinetically first, which then may lead to CIGS formation.^{241,242} It was shown that inclusion of Sb leads to formation of different Cu-Se binary phases, as well as formation of Cu_3SbSe_3 . While Cu_3SbSe_3 does not exhibit the similar electronic or crystallographic properties of CIGS, it has a low melting point similar to CuSbSe_2 and Cu_3SbSe_4 . ($\text{CuSbSe}_2 = 480\text{ }^\circ\text{C}$,²³⁹ $\text{Cu}_3\text{SbSe}_4 = 461\text{ }^\circ\text{C}$,⁷² and $\text{Cu}_3\text{SbSe}_3 = \sim 457\text{ }^\circ\text{C}$).¹³⁵ Interestingly, Cu_3SbSe_3 also demonstrates an order-disorder transition above $\sim 100\text{ }^\circ\text{C}$,^{121,122} which suggests it may act as a mobile phase and aid in the formation of CIGS at even lower temperatures than anticipated. Therefore, the proposed mechanism (figure 1.16) first includes formation of

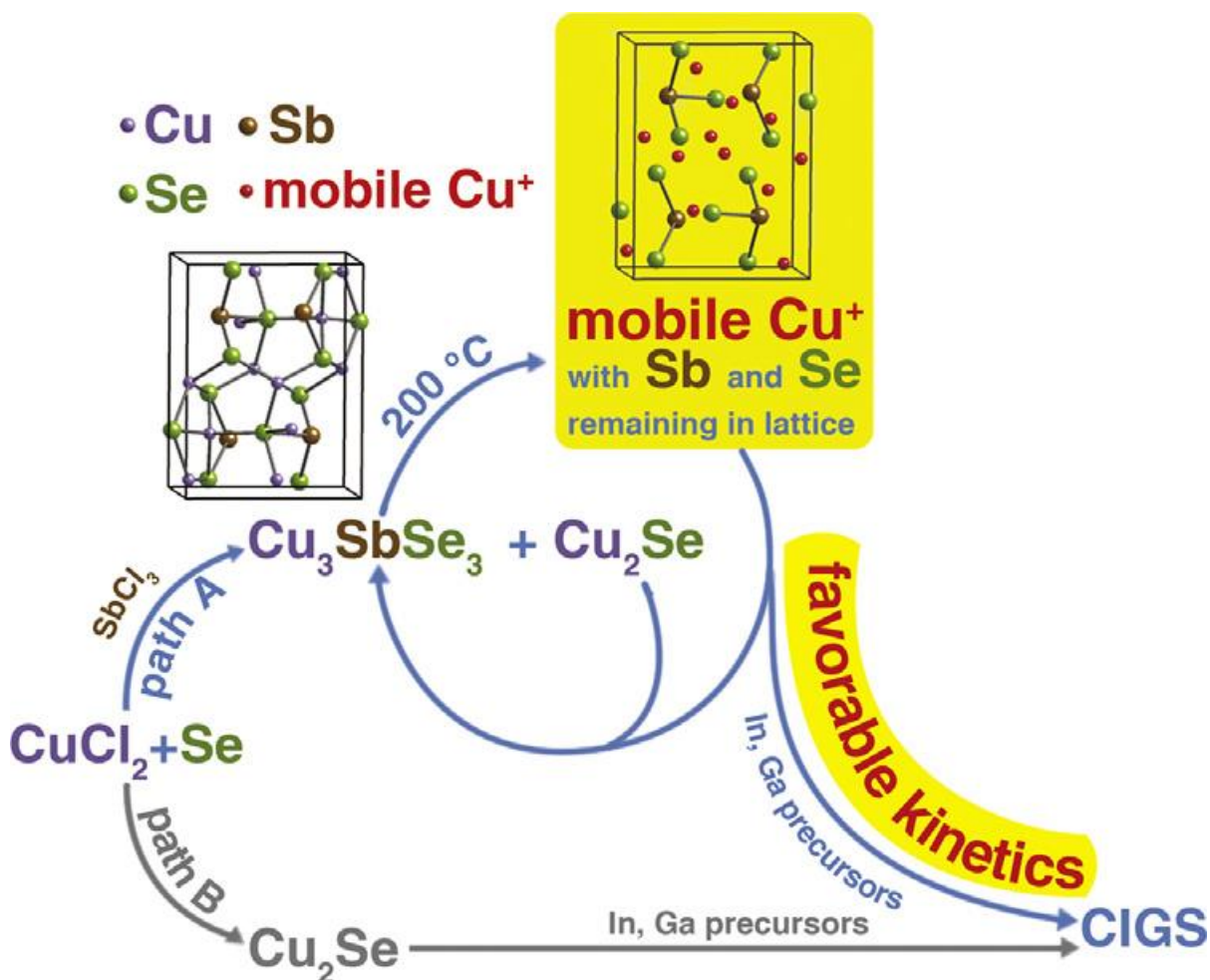


Figure 1.16 Proposed possible reaction mechanism for Sb-promoted formation of CIGS. Reproduced from reference 240.

Cu₂Se along with Cu₃SbSe₃. This is followed by reaction of mobile Cu⁺ in Cu₃SbSe₃ with In/Ga precursors to form CIGS. The Cu₃SbSe₃ is regenerated from Cu₂Se, allowing the order-disorder transition to serve as the flux for CIGS formation at exceedingly low temperature relative to molten fluxes. However, it should be noted that the arguments concerning phase diagrams and thermodynamic phases do not necessarily correspond to a solvothermal synthesis, as not only the temperature but also the pressure and the chemical potential of the solvent must also be taken into account. One other consideration for this experiment is the assertion that Cu₃SbSe₃ actually forms under the synthetic conditions, as in-situ XRD of the products under solvothermal conditions were not obtained, and Cu₃SbSe₃ may form upon cooling to room temperature.

1.11b Laser Plasma

Another application of CuSbSe₂ is as a target for laser formation of plasma. Chuchman et al. observed laser plumes formed by a low energy neodymium laser impinging upon tin and CuSbSe₂ targets. Spectra were recorded at both 1 mm and 7 mm from the target, and electron temperature as well as composition were reported.²⁴³ Later, the composition of the plumes was investigated and found to contain Sb at the front edge and the center, while Cu makes up the periphery.²⁴⁴

1.11c Other Energy Conversion and Storage Applications

We have discussed in detail the use of CuSbSe₂ as an energy conversion/generation material, but it has also been proposed as an interesting candidate for supercapacitors. Owing to its layered structure, Ramasamy et al. synthesized CuSbSe_xS_{2-x} mesocrystals via

hot injection technique.¹⁹⁴ Swift injection of sulfide precursors into copper and antimony in oleylamine yield phase pure crystals with a belt-like morphology. Tunability of the composition was achieved by controlling the ratio of 1-DDT to *t*-DDT.

Cyclic voltammetry was used to investigate the electronic properties of the material. The mesobelt morphology was found to be broken by cycling, indicative of intercalation of alkali metal ions between the layers of CuSbCh₂. Specific capacitance as high as 34 F/g was measured for CuSbSe₂, with stability of capacitance over many cycles. This is attributed to the chalcostibite layered structure. Therefore, it is of interest to demonstrate the ability to tune the interlayer gap to control intercalation of guest species throughout the channel. Using alkali metal hydroxides as electrolytes, CuSbS₂ exhibited the highest capacitance for Na⁺ whereas CuSbSe₂ demonstrates the highest capacitance for Li⁺. This confirms the value of controlling the interlayer gap distance for tuning the capacitance. Overall, CuSbSe₂ exhibits fast intercalation kinetics and good cycle lifetimes (no loss in capacitance over 5000 cycles) due to the layered structure and interlayer interactions, which render it an interesting candidate for energy storage applications.

On the energy generation side, it is also important to return to the tetrahedrite structure. No analogous selenide to the Cu₁₂Sb₄S₁₃ structure has yet been discovered or synthesized, though tetrahedrite has been well-studied for thermoelectric applications. A review of progress in this field has been written by Chetty et al. and may serve as a basis for this undertaking.¹⁷²

Despite the lack of a Cu₁₂Sb₄Se₁₃ phase, the attractive thermoelectric properties of tetrahedrite can be improved upon by exercising tunability of the composition.¹⁷¹ This was performed by achieving synthesis of Cu₁₂Sb₄S_{13-x}Se_x solid solutions where 0 < x < 3 (as

limited by Se solubility). It was determined (both theoretically and experimentally using DFT and Rietveld refinement, respectively) that Se substitution on the tetrahedral S 24g site is favored over the octahedral S 2a site.

Interestingly, substitution of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ with Se leads to increased conductivity but doesn't affect the Seebeck coefficient significantly. Further substitution to $\text{Cu}_{12}\text{Sb}_4\text{S}_{11}\text{Se}_2$ leads to a decrease in conductivity, which is possibly attributed to Se interstitial sites that can serve to scatter carriers. The maximum power factor achieved was found for the $\text{Cu}_{12}\text{Sb}_4\text{S}_{12}\text{Se}$ sample and was measured at $16 \mu\text{Wcm}^{-2}\text{K}^{-2}$ though it is noteworthy to add this sample exhibited 6.97 vol % $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ as well. Further, all Se-containing samples exhibited lower lattice thermal conductivities than the native $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ species with values of κ reaching as low as $0.33 \text{ Wm}^{-1}\text{K}^{-1}$ at 720 K for $\text{Cu}_{12}\text{Sb}_4\text{S}_{12}\text{Se}$. These combine to yield a maximum figure of merit of $ZT = 0.86$ at 720 K for the monosubstituted sample, which provides a 40% increase over the figure of merit obtained for the comparable pure $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. While this value doesn't reach as high as the doped Cu_3SbSe_4 species,^{73,82,83} it certainly demonstrates the feasibility of tetrahedrite to compete with high-ZT materials. Also, while the ZT of the Se-substituted tetrahedrite has potential for earth abundant thermoelectric applications, no selenium analogue of tetrahedrite has been reported, though it may be a promising efficient TE material.

1.12 Selenium in Solution Synthesis

Included in this review are reports that utilize a wide variety of syntheses. Typically, Cu-Sb-Se materials are synthesized in the bulk via melting of the elements followed by a quench and subsequent annealing step. For nanocrystalline materials the synthetic routes

have varied. Despite this, a common theme among many of these syntheses is that they are performed in the solution phase. While solution phase synthesis of nanostructures is common and has been thoroughly reviewed,²⁴⁵⁻²⁴⁷ it is important to the scope of the works covered here to discuss the challenge associated with formation of selenide materials through this route.

For many colloidal chalcogenide nanocrystals, sulfur is used as a facile precursor source where it can be simply dissolved in a surfactant like oleylamine under gentle or even ambient conditions. However, despite their shared membership in the chalcogenide series, selenium is often more problematic to handle synthetically.

Regardless of the dissimilarities between sulfur and selenium, the latter has found utility through a growing variety of increasingly versatile precursors. For one-pot methods, the most straightforward selenium precursor may involve simply melting selenium. Other solid selenium-containing species have been employed to this extent, such as SeO_2 ,²⁴⁸ and sodium selenite.^{249,250} A different method of decomposing selenium *in-situ* to yield metal selenide materials can be found by thermal decomposition of organometallic selenium complexes.^{251,252}

Instead of a one-pot method, many groups choose to employ the hot-injection route, typically for its high degree of control over particle size and size dispersity.^{253,254} Here, a solvated selenium species is critical. Dissolved selenium has been employed,^{28,255} often through heating above its melting point, though this requires a solvent capable of withstanding temperatures in excess of 217 °C. Further, this requires careful balance of the reaction conditions, especially with respect to the reducing character of the solution.¹⁹⁵ If this precursor is not reactive enough, other solvated selenium species exist.

Forcible reduction of selenium using a suitable reducing agent such as sodium borohydride has proven effective in the synthesis of quaternary nanocrystals.^{27,256} However, as these conditions are harsh and may etch products, other precursors are desirable. A common alternative is trialkylphosphine-selenide, in which selenium readily dissolves in trialkylphosphine with minimal effort.^{257,258} Separately, it was determined that a combination of a thiol and primary amine in the presence of selenium powder will yield a Se_8^{2-} intermediate, solvated by protonated amine. This species was first proposed as a phosphine-free selenium precursor alternative to TOPSe,²⁰⁴ though advancements were later made to include possible removal of the thiol so as to avoid sulfur contamination in the product.²⁰⁵

To avoid certain pyrophoric reagents, other complexes for selenium have been used such as dissolved selenium in paraffin oil.²⁵⁹ Other organoselenide precursors have been developed such as a selenium and dimethylamine-borane complex,²⁶⁰ selenadiazoles,²⁶¹ and diorganyldeselenide.²⁶² These reagents can be used to tune the reactivity of selenium through the strength of the selenium bonding environment.²⁶³

Another selenium precursor that is commonly used in selenium-containing colloidal nanocrystal synthesis is the reactive octadecene-selenium complex (ODE-Se).²⁶⁴ This has found application in synthesis of many widespread nanocrystalline materials, though the reactivity of this precursor is dependent upon precursor formation conditions.²⁶⁵ Further, it has been proposed that the actual reactive species from ODE-Se is actually H_2Se ²⁶⁶ akin to what has been proposed for the alkylammonium sulfur precursor.²⁶⁷ While this species has been used to some extent,²⁶⁸ it is often avoided due to the toxic nature of the compound, and difficulty with a gaseous precursor.

Finally, when comparing selenium and sulfur precursors, it is important to note that the cost of selenium is significantly increased over similar sulfur-containing compounds. For instance, while selenourea has found a degree of use in nanocrystalline synthesis,²⁶⁹⁻²⁷¹ the comparable thiourea is relatively nonhazardous and significantly less expensive.

While this list is certainly not exhaustive, it contains many of the commonly used selenium precursors for nanocrystalline synthesis. For the Cu-Sb-Se series, many of these precursors have been explored to investigate the subtle formation of these phases and to shift the solution potential to access specific favored product phases. As more becomes known about the solution-phase synthesis of Cu-Sb-Se nanomaterials, better design principles (and by extension precursor choice) may be accessed.

1.13 Conclusion and Final Remarks

Though Cu-Sb-Se materials have not achieved the same degree of success as their rare-element-containing counterparts, they still show considerable potential in the fields of thermoelectricity and photovoltaics. The figure of merit for Cu_3SbSe_4 has been steadily rising, with a maximum ZT of 1.26 reached in 2017.⁷³ Unfortunately, the low melting point of Cu_3SbSe_4 relative to other thermoelectric compounds may limit the maximum obtainable ZT for this material. The lack of an optimum preparation route for this material makes comparison difficult, though it has been shown that both nanoscaling grain sizes and doping the material lead to massive improvements in ZT. The Sb site is the most versatile dopant site, and while many dopant identities have been investigated, two directions remain of interest. First, Ti-doping was projected to yield the best results for a single dopant species,⁹⁸ but this has not yet been attempted. Second, as was shown through the champion work,⁷³

doping with multiple species can have a complementary effect, increasing the ZT higher than either species alone. Therefore, it may be worthwhile to pursue combinations of dopants to extend improvements to electronic conductivity and obtaining a measure of reduction to the already minimal thermal conductivity.

While Cu_3SbSe_4 has been explored thoroughly for thermoelectrics due to its anharmonicity, Cu_3SbSe_3 is of interest as it demonstrates an even lower thermal conductivity. This compound scatters phonons exceedingly well, in part due to an order-disorder phase transition involving mobile Cu above $\sim 100^\circ\text{C}$.^{121,122} Unfortunately, despite the desirably low thermal conductivity in this material, the electronic properties leave something to be desired, as Cu_3SbSe_3 possesses a large band gap and low carrier concentration. This could be improved with significant doping, though these studies have yet to be performed. It would be ideal to lead with calculation of optimum dopants as was performed for Cu_3SbSe_4 ⁹⁸ to determine whether adequate doping levels could be achieved and further how this might affect the electronic band structure.

Aside from thermoelectricity, Cu_3SbSe_3 has also been investigated preliminarily for photovoltaic applications. Again, the band gap is large for the optimum absorption of the solar spectrum, though preliminary work finds a suitable potential for pursuit of investigation of this compound¹³² with initial photoactivity shown for Cu_3SbSe_3 nanocrystals.¹³³

The last member of the Cu-Sb-Se family, CuSbSe_2 , is of interest for its desirable electronic properties and interesting structure. It has an optimal band gap for photovoltaics, and has been used to successfully demonstrate prototype devices achieving efficiencies up to 4.7%,¹⁸⁹ with device efficiencies improving rapidly in a short period of time. Currently,

devices are limited by the nonideal band offset between CuSbSe_2 and CdS as well as inefficiencies in optimal film thickness. While it is beginning to display appreciable power conversion efficiencies of its own, one of the great merits of CuSbSe_2 photovoltaic studies is that they demonstrate the need to broaden the scope of materials we consider in the search for alternative solar absorbers since it does not fall under the traditional chalcopyrite-type structure.

The layered structure of CuSbSe_2 has implications for improvements in cell function that would be unobtainable in the more canonical chalcopyrite structure such as saturated coordination at the surface.¹⁹¹ The layered structure is a function of the lone pair on Sb^{3+} ,⁴⁸ which is also intimately related to thermoelectric function. Unfortunately, the local geometry of Sb in CuSbSe_2 is intermediate between the tightly bound lone pair on Sb^{3+} in Cu_3SbSe_3 and the Sb^{5+} in Cu_3SbSe_4 leading to intermediate thermal conductivity⁷⁸ and ultimately low thermoelectric figures of merit.

The future direction of study for these materials is entirely reliant upon the species and application. It is our belief that Cu_3SbSe_4 should be pursued for high-efficiency thermoelectric energy generation, with an emphasis on compatible doping to improve ZT. Similarly, Cu_3SbSe_3 demonstrates such low thermal conductivities that it would make an exciting new thermoelectric material if its electronic conductivity could be increased. However, for photovoltaics Cu_3SbSe_3 doesn't absorb enough of the solar spectrum despite its initial accounts of photoactivity. Therefore, methods of decreasing the band gap through introduction of states near the band edge may be a feasible avenue for improvement. The other photovoltaic material mentioned here, CuSbSe_2 , has demonstrated preliminary device

function and as such attempts to improve these devices should focus on cell architecture optimization and engineering.

Section 1.11 has also detailed several other functions to which Cu-Sb-Se materials may be applied. The most promising of these, in our belief, is pursuit of intercalation-related applications. Owing to the layered structure, CuSbSe_2 possesses channels through which ions may diffuse, demonstrating its feasibility for applications in energy storage. It may also be useful for studies of monolayer materials, as observed with the other layered structures MoS_2 or Bi_2Te_3 . Similarly, Cu_3SbSe_3 has demonstrated a degree of ionic mobility with the mobile Cu above the order-disorder transition temperature. This may be useful as a solid electrolyte material or as a membrane/separator material. It is certainly within reason to expect there may be other applications to which Cu-Sb-Se materials pose a unique structural or electronic advantage that have not yet been explored.

Finally, in section 1.4 we have discussed the crystallography of Cu-Sb-Se materials. Though there are some copper sulfoantimonide species that do not have experimentally observed analogues, these may exist and be of use to study. Explicitly, there are three polymorphs of Cu_3SbS_3 but only the room temperature polymorph has the experimentally-determined Cu_3SbSe_3 analogue. Also, while some substitution of Se into $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ has been shown (up to $\text{Cu}_{12}\text{Sb}_4\text{S}_{10}\text{Se}_3$),¹⁷¹ the analogous selenide to tetrahedrite materials has not yet been experimentally synthesized. These phases may demonstrate enhanced properties over the well-studied sulfide phases, and further study will help elucidate a deeper understanding of formation dynamics in these materials.

While these materials have demonstrated promising function (especially Cu_3SbSe_4 for thermoelectrics and CuSbSe_2 for photovoltaics), the value of study in this system is not

limited to improvements of these specific materials. The copper-antimony-selenide species contribute significantly to our knowledge base of earth-abundant alternative inorganic materials, but also contain inherent value for the broader search for materials. Namely, the potential of CuSbSe_2 as a solar absorber inspire feasibility of layered structures that do not belong to a silicon-inspired lattice. On the other hand, Cu_3SbSe_4 supports SnSe as earth-abundant materials that may compete with rattling cages and complex crystal structures of current high-efficiency thermoelectrics. The scope of these materials merits further research, as demonstrated by the growing interest in this field. In addition to its current status of a proven capacity for thermoelectric and photovoltaic function, the Cu-Sb-Se system may find broader application as industrially, economically, and ecologically-relevant materials.

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CHAPTER 2

AMBIENT SURFACE STABILITY OF THIN FILM NANOCRYSTALLINE Cu_3SbSe_4 AND STRUCTURE-PROPERTY RELATIONSHIPS[†]

2.1 Overview

Nanocrystalline materials have a high surface area, and hence may be significantly more reactive than their bulk counterparts under ambient conditions. This may affect device function in unexpected ways. Here, high quality crystalline Cu_3SbSe_4 nanocrystals are synthesized through a hot injection route, and thin films are deposited through a ligand exchange procedure. The electronic conductivity of the films increases significantly upon exposure to air, up to $80 \text{ } \Omega^{-1}\text{cm}^{-1}$. This increase in conductivity is correlated to a surface oxidation as observed by XPS. The observed changes in the film upon exposure to ambient

2.2 Introduction

Nanomaterials are projected to be critical to future technologies, having found application in a variety of fields ranging from medicine^{1,2} to catalysis³ to energy conversion and storage.^{4,5} Because of their small size, they offer many advantages over traditional bulk materials in terms of

[†] The contents of this chapter include an article prepared and formatted for submission for publication to *ACS Applied Energy Materials*. Herein we report the synthesis of Cu_3SbSe_4 nanocrystals via a hot injection route. Subsequent observation of surface oxidation is reported and structural alterations under ambient conditions are correlated to electronic transport changes.

The initial synthesis, characterization, and manuscript preparation were performed by Daniel Agocs. Trenton Danna assisted with synthetic work. Amy L. Prieto contributed ideas, discussion, and editing help.

their processability.⁶⁻⁸ For devices incorporating these materials, the effects various fabrication processes may have on the material properties are not well understood.

Often, devices composed of nanoscale materials for electronic applications such as photovoltaics or energy storage involve simple binary crystalline materials such as CdTe⁹ or Cu₂Sb.¹⁰ While these devices are interesting, materials containing more lattice constituents may yield more tunability in function as subtle changes in composition in multinary nanocrystals can change the electronic structure and properties.¹¹ We have become particularly interested in developing synthetic methods for ternary and quaternary copper chalcogenides for applications in photovoltaics,¹²⁻¹⁷ but with increasing complexity in composition one could imagine that the surface reactivity of these materials becomes key to the overall device performance. Here, we describe the reactivity of thin films of Cu₃SbSe₄ nanocrystals, and the overall effect of those changes on the properties of the thin films.

The family of ternary copper antimony selenides are of interest for photovoltaics, however Cu₃SbSe₄ is of interest for thermoelectric energy generation. One of the major hurdles facing realization of commercially relevant modules is the scarcity of tellurium, which is present in many of the materials of interest for thermoelectrics such as PbTe, Bi₂Te₃, and Sb₂Te₃.¹⁸ This has led to a search for alternative earth-abundant materials. It is this latter class to which Cu₃SbSe₄ belongs. This material is a p-type semiconductor with a ZT_{max} as high as 1.1 at 700K.¹⁹ First prepared by Wernick and Benson,²⁰ Cu₃SbSe₄ has been investigated for its electronic structure,²¹⁻²⁵ thermal properties,²⁶⁻²⁸ elucidation of the phase diagram,^{29,30} as well as the effects of substitution³¹ and doping^{19,32-36} on its p-type thermoelectric properties. Since its original synthesis, Cu₃SbSe₄ has been prepared on the nanoscale by microwave,³⁷ chemical bath deposition,³⁸ coprecipitation,^{19,36} and hot injection^{35,39,40} methods.

One of the characteristics of nanomaterials is a large, high-energy surface area. This condition renders the material surface more reactive than the corresponding bulk phase. The reactivity of the surface has not been studied in Cu_3SbSe_4 , though Wei et al.³² note the existence of peaks corresponding to Sb-O in their X-ray photoelectron spectroscopy data which was removed by sputtering with an Ar ion source for 20 seconds. Beyond this, the effect of surface oxidation has not been studied in this material. However, to consider this material as viable for electronic transport applications, the environment in which a device will function must be considered.

To achieve a high thermoelectric figure of merit, it is desirable to minimize the thermal conductivity while maximizing the electronic conductivity and the thermopower. Therefore, while simply making materials on the nanoscale will help reduce thermal conductivity, it is also important to simultaneously ensure a high electronic conductivity. Here, nanocrystals may be detrimental as the high number of grain boundaries that contribute to decreasing thermal conductivity by scattering phonons also contribute to decreased electronic conductivity. Also, the films deposited from as-synthesized colloidal nanocrystals typically exhibit poor electronic conductivity due to the insulating ligand shell.⁴¹ However, various ligand exchange strategies have been examined to alleviate this problem in the film deposition process by improving electrical conductivity^{40,42} and also tuning the carrier concentration through doping.⁴³ Further, exchanges of organic surface capping agents with inorganic ligands that may withstand high temperatures necessary for optimum thermoelectric generation have been reported⁴⁴⁻⁴⁶.

The resulting surface of the ligand-exchanged nanocrystalline film is no longer the same as the native surface of the as-grown particles. Therefore, its interaction with the ambient environment needs to be well understood and characterized. Specifically, it is critical to elucidate how carefully controlling synthetic conditions, surface modification, and film deposition

procedures can affect the resulting properties of the material. Also, aside from the intrinsic properties of the material, the properties of the device must be characterized as a function of the ambient environment in which it will operate.

In this work, we utilize a method to synthesize monodisperse Cu_3SbSe_4 nanocrystals via hot injection similar to a previous procedure published by Liu et al.⁴⁰ Following synthesis, both inorganic and organic ligand-capped Cu_3SbSe_4 nanocrystal thin films were deposited through a dip-coating technique for subsequent electronic property evaluation by Hall measurements. The surface of the Cu_3SbSe_4 nanocrystals was analyzed for the first time, and the stability and electronic properties of the deposited films was monitored. Finally, an attempt is made to elucidate the correlation between evolution of electronic properties and variations of the nanocrystal surface structure over time.

2.3 Experimental

Materials and Methods. All chemicals were used as received, and reagent liquids were sparged with N_2 prior to use. 1-Dodecanethiol (DDT, 98+%), oleylamine (OLA, 70%), copper (II) chloride (CuCl_2 97%), antimony (III) chloride (SbCl_3 99+%), ammonium sulfide solution (20 wt.% in H_2O), and tetrabutylammonium iodide (98%) were purchased from Sigma-Aldrich. Se powder (99.99%) was purchased from Strem Chemical. Technical grade acetonitrile, toluene, hexanes (mixture of isomers), methanol, and ethanol (histological grade) were obtained from Fisher Scientific. Reaction vessels were prepared in a N_2 atmosphere glovebox. Reactions were carried out on a N_2 Schlenk line, and washing/workup was done on the benchtop.

Single Injection Synthesis. For the single injection synthesis, 0.75 mmol CuCl_2 (0.101 g) was mixed with 4 mL OLA in a 25 mL three neck round-bottom flask. Separately, 4 mL OLA was

added to a 50 mL three neck round-bottom flask containing 0.25 mmol SbCl_3 (0.057 g) and 1 mmol Se powder (0.079 g). The flasks were heated to 110 °C (at a rate of 500 °C/hour) under vacuum while stirring, and were held at 110 °C for one hour under vacuum to degas. After degassing, the flasks were both switched to positive pressure under N_2 and were heated to 200 °C. Upon reaching 200 °C, the contents of the Cu flask were rapidly injected via a 5 mL gastight syringe. Particles were allowed four hours to achieve phase purity and grow, at which point the reaction was quenched by removal of an aliquot of particles which were then washed in a small amount of toluene (<1 mL, to prevent any solidification) and excess EtOH. The particles were centrifuged at 3500 RPM for 5 minutes. The clear yellow supernatant was decanted and discarded, while the black particles were redispersed in toluene before again flocculating with EtOH and centrifuging at 3500 RPM for 5 minutes.

Double Injection Synthesis. The double injection was performed similarly to the single injection synthesis described above, though by isolating individual precursors until injection. A 50 mL three neck round-bottom flask was filled with 0.25 mmol SbCl_3 (0.057 g) and 4 mL OLA. A separate 25 mL three neck round-bottom flask was filled with 0.75 mmol CuCl_2 (0.101 g) and 4 mL OLA. Finally, 1 mmol Se (0.079 g) was dissolved in 1 mL OLA and 1 mL DDT in a scintillation vial. Using proper air-free procedure, the round-bottom flasks were transferred to a N_2 Schlenk link while the vial was sonicated to ensure complete dissolution of selenium. Flasks were heated under vacuum to 110 °C and degassed for one hour, at which point they were switched to positive pressure (N_2) and heated to 200 °C. At this temperature, the contents of the Se vial and the Cu flask were simultaneously rapidly injected into the 50 mL round-bottom, causing instantaneous nucleation of crystals as indicated by the solution changing to a black color (with a greenish hue). Particles were allowed 5 minutes to grow, whereupon the reaction was quenched

by removal of an aliquot of particles. These were then washed in a manner equivalent to that mentioned for the double injection synthesis but with a final step of suspension in chloroform and subsequent centrifugation at 3500 RPM for 5 minutes in order to precipitate any large agglomerates.

Ligand Exchange. Ligand exchange solutions were made by dissolving the 0.2 mmol exchanging ligand in methanol (15 μ L ammonium sulfide, 15 μ L ethylenediamine, 16 mg sodium sulfide, or 75 mg tetrabutylammonium iodide in 10 mL methanol). Films were dipped 30 times in the order of: 1. particles suspended in hexanes, 2. exchanging ligand in methanol, 3. acetonitrile (to remove excess ligand). Films were allowed 1 second submerged in the dipping solutions, and 1 second drying time before the next dip (dips were performed with a speed of 500 cm/min). Solutions were unaltered during the dipping process (aside from the addition of solvent to maintain a near constant volume) with the exception of the ammonium sulfide/methanol solution, which was replaced every cycle of 5 dips (~15 minutes).

Characterization. Powder X-ray diffraction (XRD) analysis was performed on a Scintag X-2 Advanced Diffraction system using Cu K α radiation ($\lambda=1.54$ Å). Samples were dropcast from hexane onto a zero background SiO₂ sample holder. Low resolution transmission electron microscopy (TEM) imaging was performed on a JEOL JEM 1400 at a working voltage of 100 keV. TEM samples were prepared by dip casting carbon-coated copper grids (200 mesh, Ted Pella) into a particle suspension in hexanes. High-resolution TEM imaging was performed on a JEOL JEM2100F at a working voltage of 200 keV. HRTEM Samples were similarly dip cast onto carbon-coated copper grids (200 mesh, Electron Microscopy Sciences). Hall measurements were recorded using a HMS-3000 Hall Effect Measurement System (Ecopia), and measurements were corrected using film thicknesses obtained by measurement on a Bruker DektakXT contact profilometer using

a cantilever pressure of 7 mg. Profilometry analysis was performed using Vision64 software. FTIR spectra of thin films were obtained with a Nicolet 380 FTIR spectrometer operating in transmission mode. X-ray photoelectron spectra were collected using a Physical Electronics ESCA 5800 system equipped with a monochromatic Al K α source ($E = 1486.6$ eV). High resolution scans were performed with a pass energy of 23.5 eV and a step size 0.10 eV/step. Data analysis was performed using Multipak version 9.3.0.3. All data were shifted to adventitious carbon (284.80 eV) in order to account for charging effects. The iterated Shirley method was used for background fitting. Crystallite size Rietveld refinements were performed using GSAS/EXPGUI.^{47,48}

2.4 Results and Discussion

Initially, we found that Cu₃SbSe₄ forms as the result of the injection of stoichiometric CuCl₂ dissolved in oleylamine (OLA) into a mixture of Se powder with SbCl₃ in OLA. In this initial reaction, particles must grow ≥ 4 hours to achieve phase-pure products. Growth times shorter than 4 hours yield a mixture of Cu₃SbSe₄ along with the binary impurity Sb₂Se₃, as seen by x-ray diffraction. Over time, there is significant Bragg peak narrowing seen in the Cu₃SbSe₄ peaks, indicating a growth in crystallite size.

We hypothesized that this growth mechanism proceeds by diffusion of copper into the Sb₂Se₃ material, similar to a report by Guria et al.⁴⁹ The presence of Sb₂Se₃ was confirmed by an XRD study of the contents of the SbCl₃/Se/OLA flask reacted under the same conditions as the injection reaction. However, products were obtained by quenching to room temperature instead of injecting copper. The product was found to be Sb₂Se₃ with no other crystalline phases present. Therefore, due to the decrease in XRD peak intensity of Sb₂Se₃ phase with growth time and

simultaneous increase in peak intensity of Cu_3SbSe_4 , we propose that the growth of Cu_3SbSe_4 proceeds through copper diffusion into the preformed Sb_2Se_3 particles. Particles grown through this copper injection exhibit size polydispersity, and are often large, with dimensions up to ~ 200 nm. The products of this reaction do not suspend, but display a high degree of crystallinity as seen through diffraction.

In order to process thin films of the Cu_3SbSe_4 , an ink suspension is desirable. Therefore, to access smaller particles, nanocrystalline Cu_3SbSe_4 was subsequently synthesized by a double injection reaction wherein Cu and Se precursors were simultaneously injected rapidly into a flask containing Sb. Immediately, black nanocrystals (with a greenish hue) nucleate, which are allowed to grow for a short period. All peaks in the XRD pattern index to Cu_3SbSe_4 , (Figure 2.1). Phase determination was also supported by SAED (Figure 2.2c).

The double injection route serves to prevent preformation of binary phases before injection by maintaining all the reactants in separate flasks, and yields phase pure Cu_3SbSe_4 with a growth time as low as 5 minutes. Particles are 11.1 ± 1.7 nm in size as measured by TEM, and exhibit good

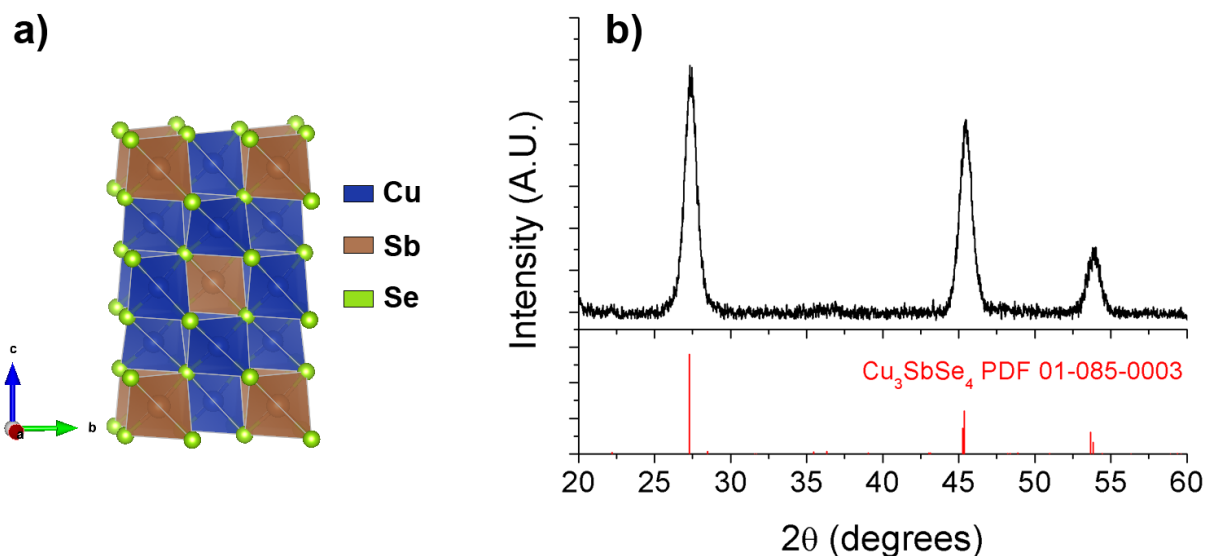


Figure 2.1 a) Structure of Cu_3SbSe_4 , which crystallizes in the Farnitine structure type, $I\bar{4}2m$. b) XRD pattern of Cu_3SbSe_4 nanocrystals, as referenced to Cu_3SbSe_4 PDF 01-085-0003.

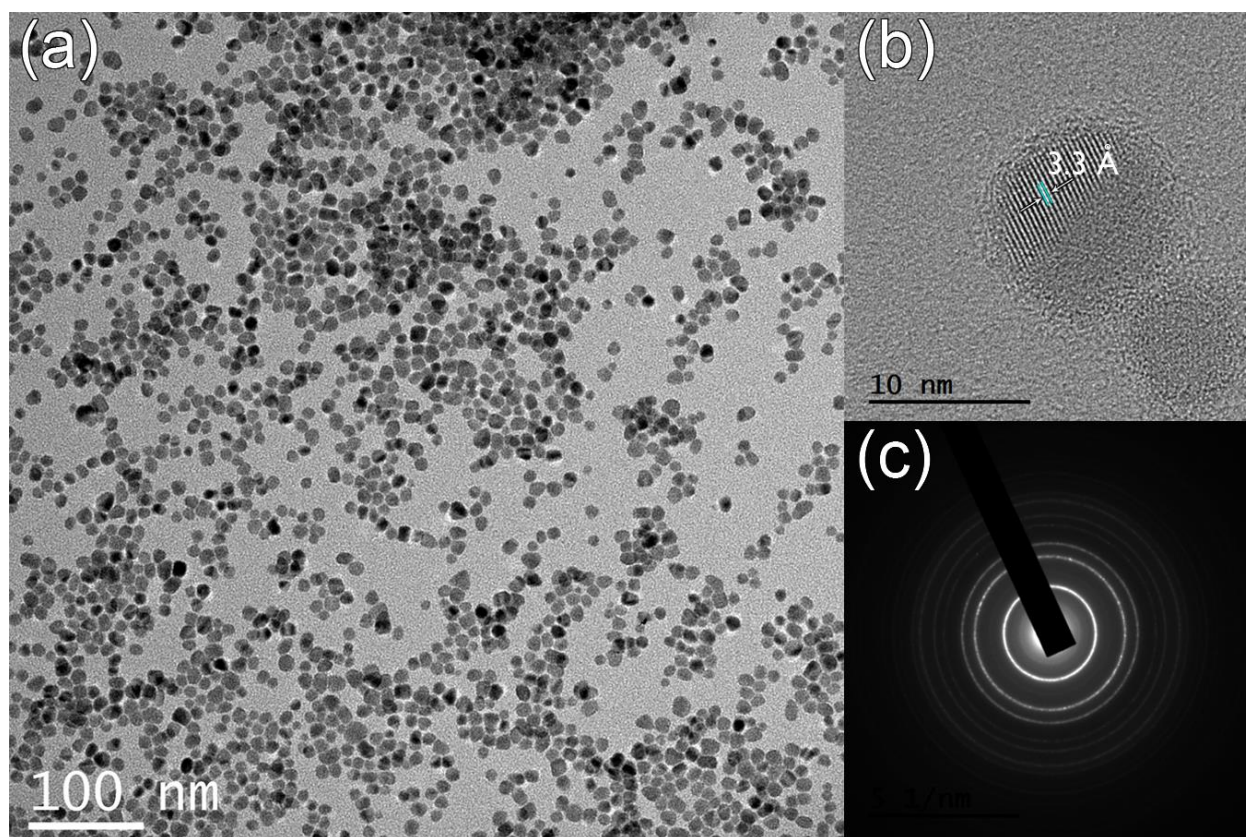


Figure 2.2 a) TEM image of Cu_3SbSe_4 nanocrystals, b) HRTEM image of single Cu_3SbSe_4 particle. 3.3 Å corresponds to the Cu_3SbSe_4 (112) plane. c) SAED pattern from ensemble of crystals.

size monodispersity (Figure 2.2a, and Figure S2.1). This allows for more regularity in controlling the properties of the material. Further, due to small crystallite size, films deposited from these nanocrystal inks contain higher number of grain boundaries that can contribute to a higher degree of phonon scattering, which has been proposed as a feasible avenue for decreasing thermal conductivity.⁶

The Cu_3SbSe_4 nanocrystals can be readily dispersed in solvents such as toluene, hexanes, or chloroform to form an ink. Therefore, thin films of the ink suspension were dipcoated in order to evaluate the suitability of Cu_3SbSe_4 nanocrystal films for thin-film thermoelectric generation. These thin films were deposited through layer-by-layer fashion employing ligand exchange reactions at each step to remove bulky ligands on the nanocrystal surface thereby improving electronic properties.⁵⁰⁻⁵² The native ligands were supplanted by both organic (ethylenediamine,

EDA) and inorganic (I^- and S^{2-}) compact ligands. Our group has previously shown these ligands to be effective for related chalcogenides.^{12,16} First a monolayer film of nanocrystals was cast on a glass substrate by dipping into the ink dispersion and then the substrate dipped in exchanging medium before finally being dipped in a separate solution of neat acetonitrile to remove excess exchanging ligands. This procedure was repeated until a film of appreciable thickness was achieved (Figures S2.6, S2.7).

Hall measurements were performed to further investigate the electronic properties of the ligand-exchanged nanocrystal films. Electrical conductivity, carrier concentration and mobility values are listed in Table 2.1. The native ligand films were not conductive, which was expected due to the large organic ligand molecules present on the surface. However, the EDA-exchanged films demonstrate a notable decrease in overall resistance. This also demonstrates the efficacy of the ligand exchange procedure. Apart from the obvious improvement in conductivity with the decrease in organic ligand chain length (OLA to EDA), the EDA-capped particles also exhibit a high carrier concentration, compared to the inorganic-capped particles. This may be due to enhanced surface recombination of holes (in the p-type Cu_3SbSe_4) with electrons (negatively charged I^- or S^{2-} ligands). This may also explain why the iodide-capped particles exhibit a higher

Table 2.1 Selected Hall properties of Cu_3SbSe_4 ligand-exchanged films.

	Conductivity ($\Omega^{-1}cm^{-1}$)	Carrier Concentration (cm^{-3})	Mobility ($cm^2V^{-1}s^{-1}$)
EDA	7.7×10^{-1}	2.0×10^{20}	6.0×10^{-2}
TBAI	1.4×10^0	7.7×10^{19}	1.2×10^{-1}
$(NH_4)_2S$	1.0×10^0	3.2×10^{19}	2.6×10^{-1}
Na_2S	8.4×10^1	1.2×10^{21}	4.2×10^{-1}

measured carrier concentration than the ammonium sulfide-capped particles, due to the increased charge density on the sulfide dianion enhancing carrier recombination.

In contrast, using Na_2S as the exchanging ligand yielded a material with the highest hole concentration. This may be due to the ability of Na^+ to cap constituent anions and minimize the electron-doping effect of S^{2-} at the surface whereas NH_4^+ or TBA^+ may be too large to participate. Further, the overall electrical conductivity obtained for these samples is exciting when placed into context of other studies on this material. Bulk Cu_3SbSe_4 typically exhibits room temperature conductivities of $\sim 50 \text{ } \Omega^{-1}\text{cm}^{-1}$,^{21,34} with a maximum up to $97 \text{ } \Omega^{-1}\text{cm}^{-1}$.⁵³ Similarly, nanocrystallite samples report values ranging from $4 \text{ } \Omega^{-1}\text{cm}^{-1}$ up to $80 \text{ } \Omega^{-1}\text{cm}^{-1}$ for a variety of syntheses and annealing/sintering methods.^{36,39,40,54} While the electronic conductivity of our thin film does not reach the maximum reported value for Cu_3SbSe_4 , it does approach the maximum achieved for a nanocrystalline sample.³⁶ This serves to support the ligand exchange as a successful strategy for tuning the electronic properties of the film, but it also demonstrates that the properties of the thin film can approach bulk values without employing an annealing/sintering step that encourages grain growth.

Though the identity of the capping ligand strongly affects the electronic properties, it is of primary interest to observe the material under the conditions in which it would likely be used for commercial application. Therefore, we studied the films after exposure to ambient conditions. Over time, it was noted that the films undergo a change, indicated by an observed difference in electronic conductivity (Figure 2.3). To measure this transformation, electronic properties were monitored over the course of two weeks.

To characterize the transport properties of the films, Hall measurements were performed at regular intervals on ligand exchanged films. Following deposition, gold contacts were

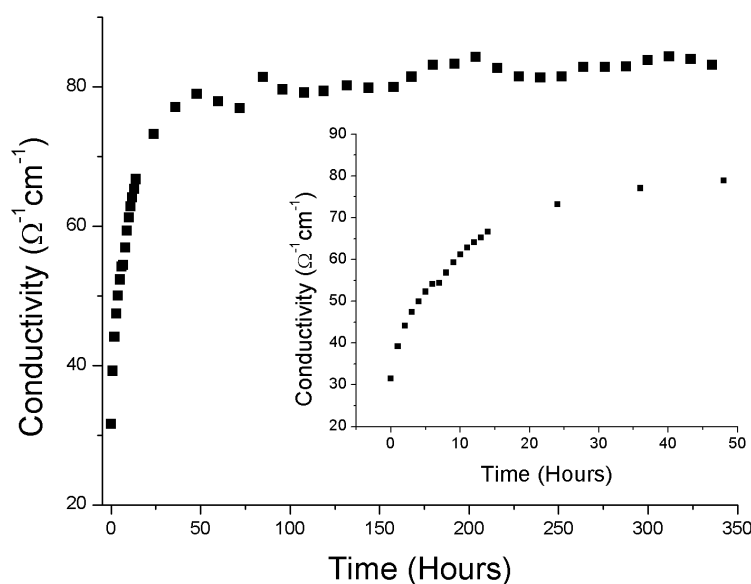


Figure 2.3 Conductivity of Na₂S-exchanged Cu₃SbSe₄ nanoparticle thin film on glass. Upon exposure to ambient conditions, the film's conductivity increases rapidly for ~48 hours. Inset is an expansion of the first 50 hours of exposure.

immediately applied to the film, which was then measured using a Hall probe. Alterations in conductivity, carrier concentration, and mobility were monitored over time and these data can be seen in Figure S2.3. It was observed that electrical conductivity increased over time with exposure to ambient conditions.

To ensure that the observed electronic property changes were due to the material's interaction with the environment instead of the gold contacts setting, we repeated this procedure, but performing the washing ligand exchange in an inert environment (N₂ glovebox) to remove the possibility of oxidation until measurements began (Figures S2.4 and S2.5). It was determined that the contacts setting may contribute a small amount to increased conductivity over the first ~5 hours, but this does not account for the total improvement in conductivity observed up to ~48 hours. It also does not account for the magnitude of the conductivity increase (~150% for the sample in air, ~60% for the sample under inert conditions, and ~1% for the sample aged before contacts).

Notably, there are two regions observed in each Hall measurement plot. The behavior of these two regions differ based on how the film is processed. First, for the film deposited on the benchtop (Figure 2.3), over the first several (~48) hours there is a marked increase in electrical conductivity while the film reacts with the ambient environment. For a p-type semiconductor such as Cu_3SbSe_4 , conductivity is related to intrinsic electronic properties through the relationship $\sigma = pe\mu_h$ where σ is the conductivity, p is the concentration of holes, e is the elementary charge, and μ_h is the hole mobility in the material. The increase in conductivity in this first region is due to the hole mobility, which is observed to increase during this time (Figure S2.3). After a period of about two days (though this time depends upon the thickness of the individual film), the film reaches a plateau of about $80 \text{ } \Omega^{-1}\text{cm}^{-1}$, indicating that the film has completed its reaction with the environment. To ensure complete reaction, the film was monitored over the course of two weeks. After the increasing regime, the film maintains constant conductivity and mobility within error.

On the other hand, for films deposited under inert conditions, a distinct behavior is observed. The first region (increasing conductivity due to increasing mobility) reaches a peak ~12 hours after exposure to air. The second region (>48 hours of exposure) exhibits a linearly decreasing conductivity, though the slope is small. We hypothesize that the film dipped in air allowed exposure of all layers of the film to oxidize, effectively hole-doping the material whereas the films deposited under inert conditions only interact with the environment at the surface, leading to a lesser degree of hole-doping. This is observed by monitoring the carrier concentrations obtained for each sample as a function of time (Figure S2.4).

Though we have established that the electronic conductivity of the films increases upon exposure to ambient conditions, it is also necessary to understand how the films change chemically. To do this, X-ray photoelectron spectra were obtained of the Na_2S ligand-exchanged films (Figure

2.4). XPS fitting data can be found in Figure S2.10. The as-synthesized sample clearly exhibits one Cu environment, two Sb environments, and one Se environment. Interestingly, this is one area in which there has been debate in the literature, particularly surrounding the valence state of Sb.^{24,26,28} To elucidate this, there have been reports using X-ray absorption near edge structure,⁵⁵ bonding arguments,²⁸ and XPS^{32,38,40,56} to identify the composition of Cu_3SbSe_4 . While XPS is a thorough and comprehensive technique, there are still discrepancies observed in the obtained spectra. Our typical spectra demonstrate that Cu exists as Cu^+ , Sb as Sb^{5+} , and Se as Se^{2-} , all with one oxidation state.^{40,56} However, Ghanwat et al. report the presence of a Cu^{2+} species,³⁸ while Wei et al. observe a peak corresponding to Sb-O at the surface.³² These reports demonstrate the

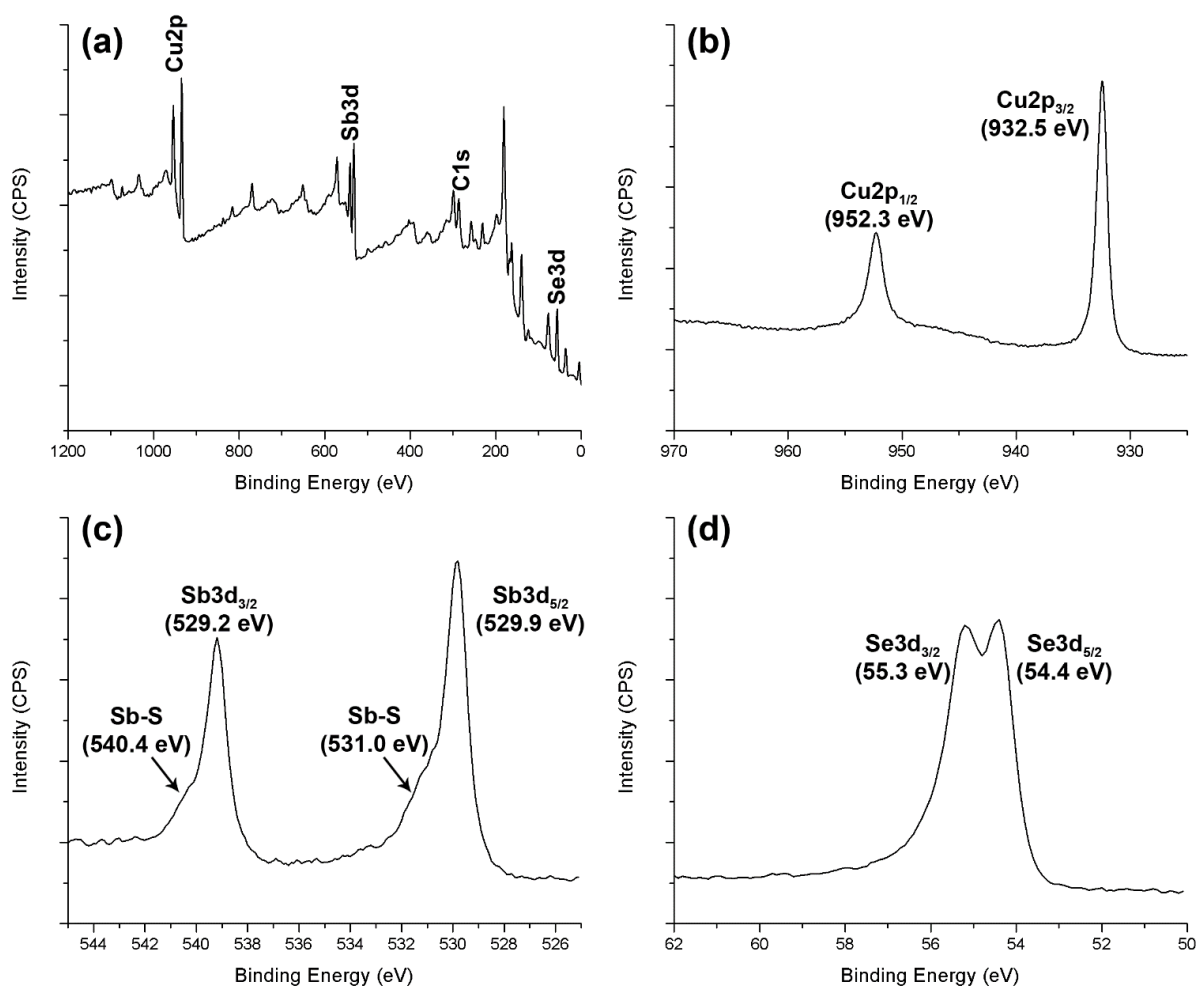


Figure 2.4 X-ray photoelectron spectra of Na_2S -exchanged Cu_3SbSe_4 nanocrystals: a) survey scan, b) Cu2p, c) Sb3d, and d) Se3d peaks.

surface reactivity of Cu_3SbSe_4 , with the latter work unambiguously characterizing the Sb-O as a surface state by its removal via Ar-ion milling.

Our results support the oxidation states of the constituent elements being Cu^+ , Sb^{5+} , and Se^{2-} as expected. This is also supported by native valence counting and the lack of any satellite peaks in the Cu2p spectrum. This spectrum exhibits two peaks with the $\text{Cu}2p_{1/2}$ peak at a binding energy of 952.3 eV and the $\text{Cu}2p_{3/2}$ peak at a binding energy of 932.5 eV, which are in good agreement with literature values of Cu^+ species with similar coordination (Cu- Se_4 tetrahedra) such as CZTS⁵⁷ and CIGS.^{58,59} The Sb spectrum demonstrates a set of peaks of high intensity at 539.2 eV and 529.9 eV for the $\text{Sb}3d_{3/2}$ and $\text{Sb}3d_{5/2}$, respectively. These peaks index to the intrinsic Sb-Se tetrahedra. There are also shoulders at the higher binding energies 540.4 eV and 531.0 eV. We propose that these peaks correspond to the Sb-S surface of the Cu_3SbSe_4 nanocrystals, as Sb-S is expected to exhibit a peak at a higher binding energy than Sb-Se. This sulfur inclusion is due to either any unremoved native dodecanethiol ligands on the crystal surface or from the Na_2S ligand exchange. Finally, the Se3d spectrum exhibits the expected overlap of $\text{Se}3d_{3/2}$ and $\text{Se}3d_{5/2}$ at 54.4 eV and 55.3 eV, respectively. These peaks are relegated to the native Se environment in the lattice, which is composed of Se coordinated to three Cu and one Sb each.

Following exposure to the ambient environment, the film exhibits structural changes which are reflected in modified electronic properties. Analysis of the XPS taken with 96 hours of oxidation shows several significant differences when compared to the unexposed sample (Figure 2.5). The Cu2p spectrum shows the appearance of a higher binding energy set of peaks that correspond to Cu^{2+} , which is corroborated by the appearance of satellite peaks. A Cu^{2+} species is consistent with the XPS data reported for nanocrystalline Cu_3SbSe_4 which shows the existence of both mono- and divalent copper species present.³⁸ Further, the Sb3d spectra shows what first

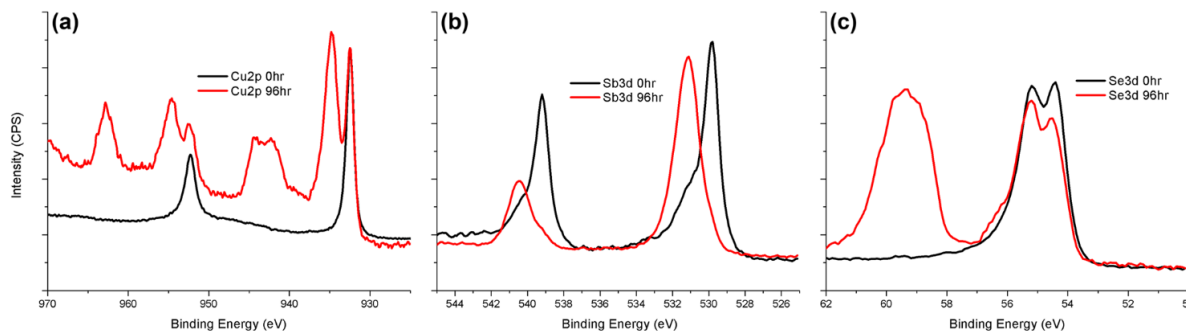


Figure 2.5 XPS spectra showing the native crystal (black), and the material as exposed to air for 96 hours (red). Significant oxidation events can be seen in a) Cu2p (Cu^+ to Cu^{2+}), b) Sb3d (Sb-O), and c) Se3d (SeO_2) spectra.

appears to be an apparent shift to higher binding energy. However, fitting of the data instead shows the peak at 539.2 eV remains at the same binding energy, but there is the appearance of a new peak at 540.5 eV which we attribute to Sb-O as a product of exposure conditions. For proper analysis of the Sb3d spectra, the Sb3d_{3/2} peaks are used, as O1s overlaps the Sb3d_{5/2} binding energies, significantly convoluting the fitting. Finally, the Se3d spectrum exhibits the representative overlapping peaks at 55.3 eV and 54.4 eV, indicative of the native crystal's Se environment. However, there is the appearance of two features of interest in this spectrum. First, there is the inclusion of a large peak at much higher binding energy (59.3 eV) that we attribute to the formation of SeO_2 . Further, there is the growth of a shoulder at slightly higher binding energy (55.7 eV) than the native Se peaks. The shoulder matches well with a pair of peaks that we index to Se coordinated to the oxidized Cu^{2+} .

The chemical data obtained from the XPS supports a model in which the as-synthesized nanocrystals undergo specific oxidation, which can be used to rationalize the observed changes in electronic conductivity. Upon exposure to air, some Cu^+ oxidizes to Cu^{2+} (likely coordinated to oxygen at the surface). Similarly, Sb coordinates at the surface to form Sb-O in place of the native Sb-Se or ligand-exchanged Sb-S. This surface effect is corroborated by a previous work which observed the presence of the Sb-O species, and noted it could be removed by Ar ion milling, confirming the presence of this species only at the surface of the film.³² Simultaneously, Se readily

oxidizes to form SeO_2 . These three events occur in the presence of oxygen, which may serve as the reduced species from diatomic O_2 or moisture in the air.

The oxidation of a material with Cu-Se coordination may serve as a hole dopant, as has been observed previously in the literature for Cu_2Se nanoparticles.⁶⁰ In addition, the formation of SeO_2 may serve as an amorphous surface coating, as this phase is not observed in the X-ray diffraction pattern. The resulting strain at the surface may aid in hole mobility.⁶¹ This, in conjunction with the possibility of hole doping from the copper oxidation, may serve to explain the increase observed in electronic conductivity. It is possible that the oxidation of copper proceeds beyond the ideal hole doping concentration, or that the SeO_2 surface may be too thick over time that the electronic conductivity drops after the initial rise. Further, in analysis of the material, the XPS spectra of a sample aged for two weeks indicates no changes from the spectra obtained after 96 hours, indicating that the oxidation is complete by the end of the initial conductivity drop observed from Hall measurements.

2.5 Conclusions

In this report we detail the synthesis of Cu_3SbSe_4 nanocrystals through a hot injection method and the subsequent preliminary characterization of their electronic properties. The identity of reactant species was found to be critical to the synthesis of suitable nanocrystals, where a double injection of Cu and Se precursors yields the most robust route. It was determined that monodisperse nanocrystals of p-type Cu_3SbSe_4 could be easily ligand exchanged and deposited as thin films. Ligand-exchanged particles exhibit good initial electronic properties such as high conductivity ($8.4 \times 10^1 \text{ } \Omega^{-1}\text{cm}^{-1}$), good hole mobility ($4.2 \times 10^{-1} \text{ cm}^2/\text{Vs}$), and high carrier concentrations ($1.2 \times 10^{21} \text{ cm}^{-3}$). Of all ligands tested, Na_2S -exchanged particles demonstrate the

best electronic properties. We found that films oxidize under ambient conditions over the course of two days, improving their electronic properties, and these improvements were stable over time. The changes in electronic conductivity are likely due to a surface oxidation. We have demonstrated initial electronic properties of these Cu_3SbSe_4 nanocrystals, and suggest that they may be feasible in conjunction with appropriate ligand exchanges for application in thermoelectric devices.

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CHAPTER 3

HOT-INJECTION ROUTE FOR SYNTHESIS OF Cu_3SbSe_3 NANODISCS AND INVESTIGATION OF STRUCTURAL ANISOTROPY[†]

3.1 Overview

Earth-abundant alternative materials for photovoltaic applications are of interest due to their potential for lowered economic expense and environmental impact. The family of $\text{Cu}_x\text{Sb}_y\text{Se}_z$ compounds are of particular interest because some members of this family have direct band gaps, and potentially large absorption coefficients. Herein we describe a hot injection route to synthesize nanodiscs of Cu_3SbSe_3 . Our synthetic method yields nanodiscs that measure 12 nm in diameter and 3 nm thickness, with disc faces along the (200) plane. Some preliminary alignment of particles has been observed, which may lead to improved electronic coupling of particles and mitigation of recombinatory losses in assembled photovoltaic devices.

3.2 Introduction

Current generation two photovoltaic technologies employ absorber materials such as CdTe and $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS). These two materials contain rare constituent elements such as indium

[†] The contents of this dissertation chapter include an article prepared for submission to *Nano Letters*. We report the synthesis of Cu_3SbSe_3 nanodiscs via a hot-injection approach. Initial optical and photoelectrochemical results are reported, as well as a brief investigation of the interesting morphology exhibited by the material.

The initial synthesis, characterization, and manuscript preparation were performed by Daniel Agocs. Josie Hendrix assisted with synthetic work and ideas concerning nanodisc stacking. Amy L. Prieto contributed ideas, discussion, and editing help.

and tellurium, which has engendered a search for feasible earth-abundant photovoltaic absorbers.^{1,2} Of these, $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ (CZTS) has emerged as the forerunner for earth-abundant alternatives to CdTe and CIGS.^{3,4} Efficiencies of up to 12.6% have been achieved by a hydrazine-based pure solution approach.⁵ However, despite initial promising success, CZTS is plagued by traditionally low open-circuit potentials likely due to cation disorder.⁶ This begets the need for exploration of alternative earth-abundant photoabsorber materials that are not as prone to disorder that can result in energy levels in the band gap.

One proposed alternative material, Cu_3SbSe_3 , fits many of the desirable traits for photoabsorbers. It has a band gap feasible for absorption of the solar spectrum⁷⁻¹¹ (although it has not yet been evaluated for full-cell photovoltaic performance) and it is composed of earth-abundant elements. Another beneficial characteristic of Cu_3SbSe_3 is the potentially simpler structure relative to CZTS. This is especially manifest in the defect profiles of these two materials, where Cu_{Zn} and Zn_{Cu} antisites are known to readily form in CZTS^{12,13} whereas Cu_3SbSe_3 contains cations with significantly different sizes that these defect formation energies should be much higher, though nobody has studied this yet. Further, some degree of tunability has already been achieved in the Cu_3SbSe_3 system with band gaps ranging from 1.58-1.85 eV by annealing,⁹ or from 1.38-1.84 eV by utilizing a mixed chalcogenide stoichiometry $\text{Cu}_3\text{SbS}_x\text{Se}_{1-x}$.¹⁰ Theoretical predictions also support the potential for photovoltaic application of this material and suggest the need for further investigation.⁸

The Cu_3SbSe_3 phase has previously been synthesized on the nanoscale, first reported by hot injection using a dimethylamine borane selenium precursor.¹¹ However, in our hands this synthesis did not yield controllable results. A second nanocrystalline hot injection synthesis was reported using a selenium diazole precursor, though the resulting crystals are polydisperse and the

optical band gap is larger than expected for Cu_3SbSe_3 .¹⁴ Therefore, we aim to develop an alternative synthesis of Cu_3SbSe_3 that exhibits control over phase composition, and particle size (while maintaining size monodispersity). Further, we wish to provide preliminary evaluation of our material for photovoltaic applications, as Cu_3SbSe_3 has been proposed to be a good photovoltaic material^{7,8} though there are a limited number of experimental works appraising Cu_3SbSe_3 for this application.⁹⁻¹¹ Also, we have determined that our synthetic conditions lead to interesting morphology in the as-synthesized Cu_3SbSe_3 nanostructures which may be utilized to circumnavigate some of the problems with conventional photovoltaics. Morphological control of binary nanocrystals is a relatively well-established field,¹⁵⁻¹⁷ though this does not easily transfer to ternary materials due to a significant increase in crystalline complexity.

Here, we present an alternative synthesis using the reduced Se cluster method^{18,19} as a reactive precursor. This synthesis potentially yields a method to avoid contamination of the particles by phosphorus (as trioctylphosphine precursors may exhibit), boron (from dimethylamine borane), and thiols. Despite concerns about the stability of dodecanethiol at high temperatures,¹¹ here we observe no discernable sulfur incorporation into the Cu_3SbSe_3 structure, while showing that the dodecanethiol plays an important role in particle morphology which may lead to profound advances for the field of photovoltaic colloidal nanocrystals as will be discussed below.

3.3 Experimental

Materials and Methods. All solids and washing solvents were used as received. Oleylamine and dodecanethiol were sparged 2 hours using N_2 to degas prior to use. All chemicals were used as received, and reagent liquids were sparged with N_2 prior to use. 1-dodecanethiol (DDT, 98+%), oleylamine (OLA, 70%), copper (II) chloride (CuCl_2 97%), antimony (III) chloride

(SbCl₃ 99+%), and ethanethiol (97%) were purchased from Sigma-Aldrich. Se powder (99.99%) was purchased from Strem Chemical. Technical grade acetonitrile, toluene, hexanes (mixture of isomers), methanol, and ethanol (histological grade) were obtained from Fisher Scientific. Reaction vessels were prepared in a N₂ atmosphere glovebox. Reactions were carried out on a N₂ Schlenk line and washing/workup was done on the benchtop.

Synthesis of Cu₃SbSe₃ nanodiscs. In a typical synthesis, 0.75 mmol CuCl₂ and 0.33 mmol SbCl₃ were added to a 50 mL three-neck round bottom flask, which was equipped with a thermocouple, reflux condenser, and stir bar. To this flask was added 4 mL oleylamine to act as a reaction medium and solvent. In a separate scintillation vial, 0.75 mmol Se was dissolved in 1 mL oleylamine and 3 mL dodecanethiol.¹⁸ The metals flask was heated to 110 °C under vacuum, at which point it was held for one hour to degas. While the metals flask degassed, the Se vial was sonicated to ensure complete dissolution (a dark red liquid was obtained, indicative of Se₈²⁻)¹⁹. After the degassing period, the metals flask was switched to positive pressure under N₂ and was heated to 150 °C. After a short period (~5 minutes), the solution becomes a yellowish orange color, indicating complexation of Cu with oleylamine. At this point, the contents of the Se vial were rapidly injected into the metals flask via gastight syringe. The solution immediately forms a brown product, which was allowed five minutes to grow at 150 °C. After five minutes, the growth was quenched by removal of particles for washing.

Particles were washed by addition of ~1 mL toluene (to prevent solidification of long alkyl chains) and ~8 mL ethanol as antisolvent to encourage precipitation with subsequent centrifugation at 3500 RPM for 5 minutes. The faint yellow supernatant (consisting of unreacted precursors and excess organic reaction media) was decanted and discarded. The precipitated brown particles were redispersed in toluene and sonicated to encourage thorough washing before

centrifuging again at 3500 RPM for 5 minutes. The clear, colorless supernatant was again decanted and discarded. The particles were resuspended in chloroform, sonicated, and were finally centrifuged one last time at 3500 RPM for 5 minutes. Large agglomerates precipitate, but suspended particles are used for subsequent characterization.

For reactions assessing the impact of dodecanethiol on Cu_3SbSe_3 nanodisc synthesis, alternative precursors were employed though the synthetic procedure remains the same as described above. The screened injected species are as follows: sodium selenium dispersed in oleylamine, trioctylphosphine selenide, molten selenium (heated to 230 °C in oleylamine), sodium borohydride (mixed with selenium in oleylamine to dissolve), and volatile thiol (selenium mixed with oleylamine and ethanethiol were heated under vacuum on a hotplate at 100 °C to remove any of the formed diethanedithiol). These species were injected into the metals flask after it had been degassed. Similarly, trioctylphosphine selenide was addressed as an injected species into a trioctylphosphine oxide solution, wherein the solvent in the metals flask was 10 mmol trioctylphosphine oxide, though again the procedure follows that described above. After each injection, particle washing proceeded as has been described above for the typical synthesis of Cu_3SbSe_3 nanodiscs.

Characterization. Particles were first analyzed by x-ray diffraction (Bruker D8, Cu $K\alpha$ radiation, $\lambda=1.54 \text{ \AA}$) to ensure phase purity. Transmission electron microscopy was performed using a JEOL JEM 2100F microscope operating at 200 keV accelerating voltage. UV-Visible spectroscopy was performed on an Agilent 8453 UV-Visible spectroscopy system. Hall measurements were recorded using a HMS-3000 Hall Effect Measurement System (Ecopia). Photoelectrochemical testing was performed using a CH Instruments 1230A potentiostat in conjunction with a 65 W Xe arc lamp as a white light source. To simulate the solar spectrum, the

lamp beam was filtered using a visible wavelength bandpass filter (Thorlabs, KG3, ~315-710 nm) as well as a 400-nm long-pass filter. The lamp power was adjusted using a ThorLabs S302A thermal power sensor.

Solid-Phase Ligand Exchange. To modify the surface of the nanodiscs, solid-phase ligand exchange was performed. Ligand exchange solutions were made by dissolving 0.2 mmol exchanging ligand in methanol (16 mg sodium sulfide in 10 mL methanol). Films were dipped 30 times in the order of: 1) particles suspended in hexanes, 2) exchanging ligand in methanol, 3) acetonitrile (to remove excess ligand). Solutions were unaltered during the dipping process (aside from the addition of solvent to maintain a near constant volume).

3.4 Results and Discussion

Synthesis of Cu_3SbSe_3 nanodiscs was achieved by the hot injection route, as it provides precise control over composition, morphology, and dispersity. In a typical synthesis, CuCl_2 , SbCl_3 , and oleylamine (OLA) were combined under inert conditions, and were subsequently heated to 110 °C under vacuum. After holding at 110 °C for an hour to degas, this solution was heated to 150 °C under N_2 , where it was held until an orange color was obtained (indicating complexation of Cu with oleylamine). Simultaneously, Se powder was dissolved in a mixture of oleylamine and dodecanethiol (DDT), and was sonicated to ensure complete dissolution. To initiate nucleation, the Se/OLA/DDT was rapidly injected into the hot metals solution. Immediate formation of brown product was noted, and particles were allowed five minutes to grow. Nanocrystalline growth was quenched by removal of product into a separate container, and particles were washed several times before a final resuspension in chloroform.

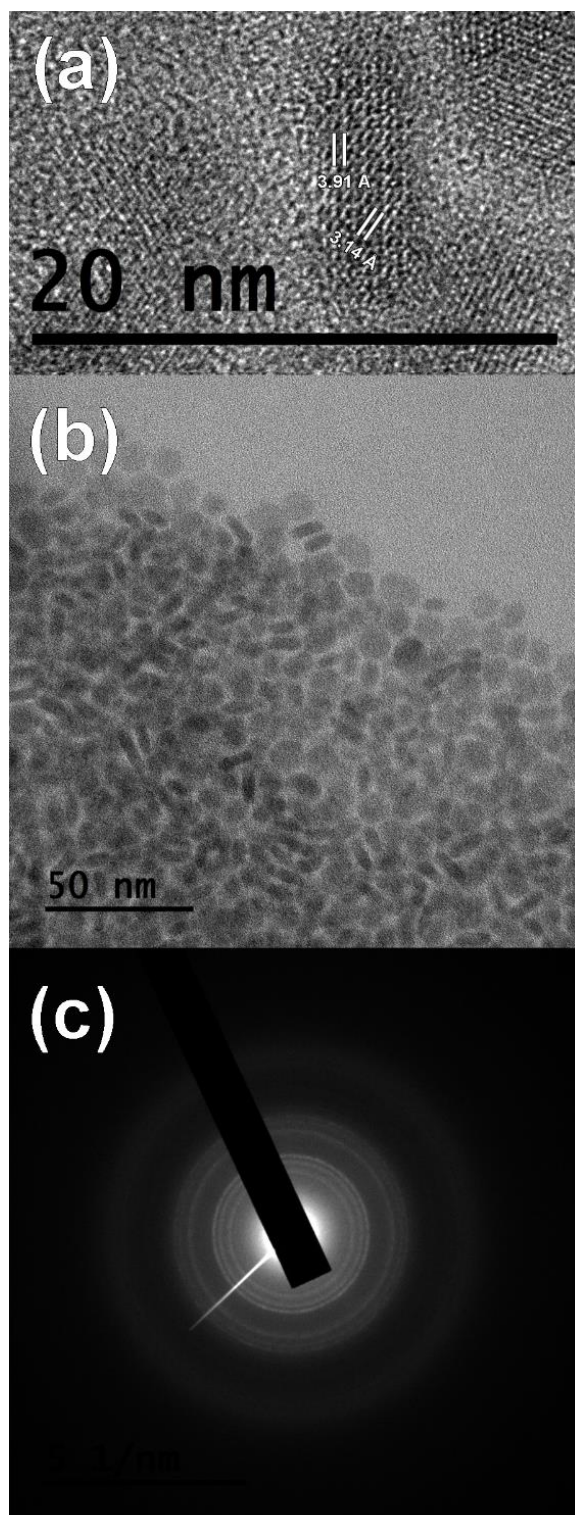


Figure 3.1 TEM images of Cu_3SbSe_3 nanodiscs: a) HRTEM image showing (200) lattice planes parallel to disc faces (3.91 Å), b) nanodiscs have a diameter of 11.2 ± 1.2 nm and a thickness of 4.0 ± 0.3 nm, and c) selected area electron diffraction pattern of the nanodiscs.

A representative transmission electron micrograph (TEM) of the as-synthesized Cu_3SbSe_3 nanodiscs is presented in Figure 3.1. The disclike morphology of the particles leads this material to self-assemble (to a small degree) into stacks of particles arranged face-to-face. This stacking is of particular interest as it poses a potential method of increasing exciton diffusion lengths as has been reported with CdSe nanoplatelets.²⁰ Furthermore, if the nanodiscs self-assemble into large columns with epitaxial arrangement, exciton recombination at grain boundaries may be lowered by the existence of a larger effective crystallite size while retaining the low-cost processing afforded by the formation of a nanocrystalline ink.

The origin of particle morphology is critical to understanding nanodisc stacking, and by extension the development of rational design strategies to optimize particle assembly. Initially, high resolution transmission electron microscopy (HRTEM) images were used to measure lattice spacings of 3.88 Å parallel to the disc faces, which correlate well with the accepted value of 3.99 Å for the (200) face for orthorhombic Cu_3SbSe_3 (Figure 3.2).²¹ The observation of the disc face being the (200) plane provides insight into the morphology-directing agent of this synthesis. As shown in figure 3.2, the (200) plane of Cu_3SbSe_3 is Se-rich. We hypothesize that the coordination

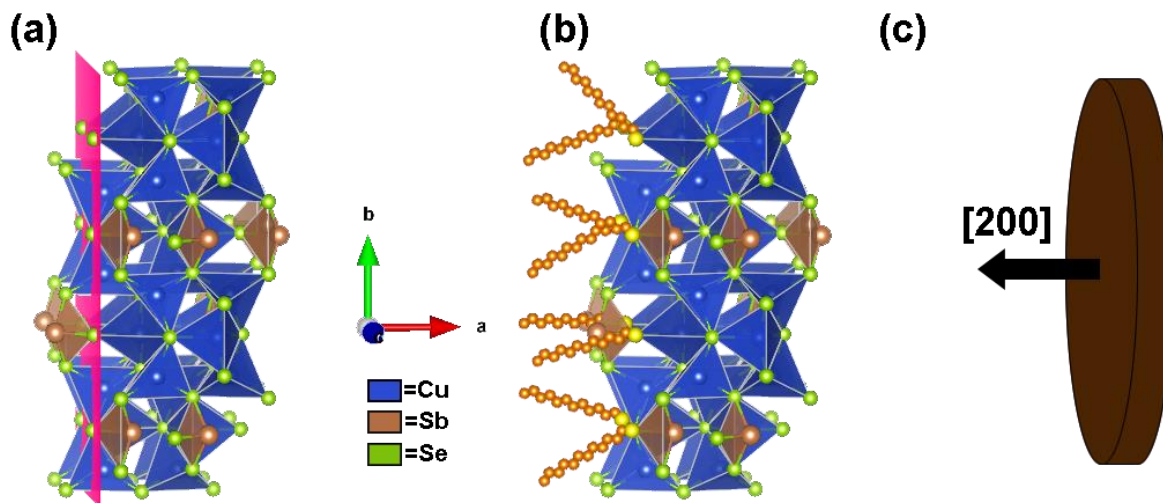


Figure 3.2 Crystal structure of orthorhombic Pnma (62) Cu_3SbSe_3 , with 0.5-1.5 unit cells in the a direction, 0-2 in the b direction, and 0-2 in the c direction. The pink plane in (a) demonstrates the (200) plane, while (b) suggests the binding of dodecanethiol on Se sites along the (200) plane. The [200] direction is shown in (c), demonstrating the morphology of the nanodiscs.

of the specific organic surfactants present during crystal nucleation and subsequent growth leads to the observed disclike morphology. Following the initial nucleation of the Cu_3SbSe_3 phase, surfactants coordinate to high-energy facets of the nanocrystals.²² It is our belief that oleylamine acts to suppress rapid growth of the particle size, while dodecanethiol more strongly coordinates to Cu and Sb on the (200) face in Se positions. As oleylamine still constitutes a large portion of the organic reaction media in these reactions, it's likely that the surface capping would be similar. On the other hand, effectively diluting the concentration of oleylamine may serve to decrease its ability to stabilize the surface of the crystals during nucleation, leading to faster growth and larger particle sizes. The other ligand used, dodecanethiol, may coordinate more strongly to the specific facets in the Cu_3SbSe_3 nucleated seeds. This would drive growth in the *b*- and *c*-directions, but limit it in *a*, which would yield a disclike morphology such as those demonstrated here.

To test this hypothesis, a synthesis was performed using different Se precursors to avoid the presence of the thiol. We determined that the presence of phosphines yields crystalline Sb metal, and reducing Se to the Se^{2-} oxidation state with sodium borohydride results in a mixture of several crystalline products, though no Cu_3SbSe_3 was observed (XRD results of thiol-free Se precursor reactions are available in the supporting information). Interestingly, simply using a mixture of Se and oleylamine yields a bright orange precursor that has been used in other nanocrystal syntheses,^{23,24} and resulted in formation of Cu_3SbSe_3 nanocrystals. This reaction yields a product that exhibits a somewhat broader peak than expected around $27^\circ 2\theta$, though the presence of Cu_3SbSe_3 is clearly confirmed. In order to observe morphology of the Se/OLA nanocrystals, TEM micrographs (Figure 3.3) were obtained in which some of the particle exhibit faceting. Of interest, despite particles looking like they may be discs lying flat against the grid, no stacking is observed leading us to believe these circular particles are isotropic spheres which

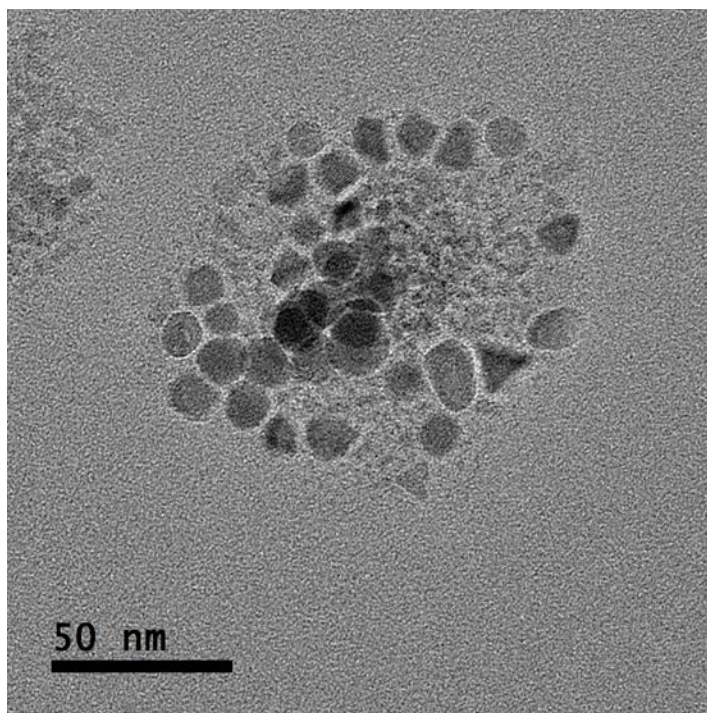


Figure 3.3 TEM image of Cu_3SbSe_3 nanocrystals synthesized using Se/OLA to avoid morphological influence of the thiol. Some particles exhibit faceting, and no stacking is observed.

may form as a result of weaker ligand coordination to the surface during crystal growth. These nanocrystals' size is also worthy of noting, as they are similar to the diameter of the nanodiscs, indicating that perhaps oleylamine is responsible for size control while dodecanethiol influences morphology.

One final thiol-free experiment was performed in order to observe the effect of the thiol moiety on nanodisc morphology. To ensure similar reactivity of the Se precursor, anionic selenium was prepared in a mixture of ethanethiol and oleylamine in the manner of Walker and Agrawal.¹⁹ Ethanethiol has a low boiling point, and can be removed using gentle heating with vacuum resulting in a thiol-free selenium precursor formed through the same method as the dodecanethiol-oleylamine reduction of selenium. Instead of crystalline Cu_3SbSe_3 , this reaction surprisingly produces a mixture of Cu_3SbSe_4 and $\text{Cu}_{1.8}\text{Se}$ (Figure S3.1).

Further support for the (200) plane being the face of the disc was found using scanning transmission electron microscopy (STEM) diffraction results. Here, an area was observed where some particles stack and some do not. Diffraction images were obtained for particles stacked (on their sides) and unstacked (lying flat) on the grid. These results are shown in Figure 3.4. The diffraction patterns obtained from discs lying flat on the grid index well to the diffraction pattern observed looking down the (a00) direction, supporting the lattice spacing measurement.

X-ray diffraction (XRD) was also performed on the synthesized nanocrystals. Phase-pure nanodiscs were obtained from particles suspended in chloroform. Interestingly, the XRD patterns exhibit preferred orientation, which is expected for discs as they are most likely to lie flat against the substrate. However, often in more concentrated areas of a sample the sheer number of particles may arrange such that nanodiscs are forced into a position perpendicular to the substrate, as shown in figure 3.1b (it is important to note that the particles reported in this figure are products of the double injection synthesis reported in chapter 4). Increased signal is seen for the 200 peak in the diffraction pattern relative to other peaks, and this signal can be increased by dilution of the

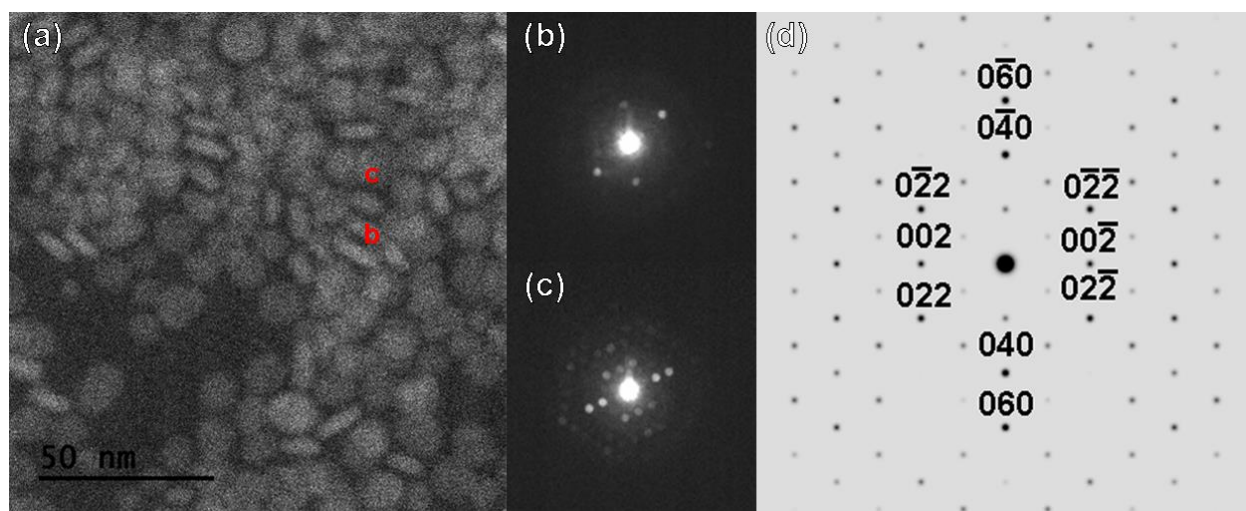


Figure 3.4 STEM diffraction of Cu_3SbSe_3 nanodiscs: a) dark field STEM image of particles, b) diffraction pattern of stacked particles, c) diffraction pattern of flat particle, and d) single crystal diffraction spots along the [a00] zone axis indexed to hkl values. Flat particles match the single crystalline pattern of the [a00] direction and differ from the pattern found in stacked particles.

suspension prior to drop casting, supporting that the particles will lie flat against the substrate if allowed.

Preliminary optoelectronic properties were measured for the Cu_3SbSe_3 nanodiscs to aid in assessment of their photovoltaic potential. The observed band gap of the nanodiscs is found to be 1.56 eV, and the data is indicative of an indirect gap as seen in figure 3.5. This is interesting as reports of Cu_3SbSe_3 have determined both indirect²⁵ and direct^{9,11} band gaps in this material. Further, this result falls within the range of values predicted by DFT calculations.^{7,8} Though the band gap is slightly larger than the ideal value for photovoltaic energy conversion, we were still able to observe photocurrent in a Schottky barrier device. The observed photocurrent (Figure 3.6) is significant and may be improved in the future as no optimization was performed in this study.

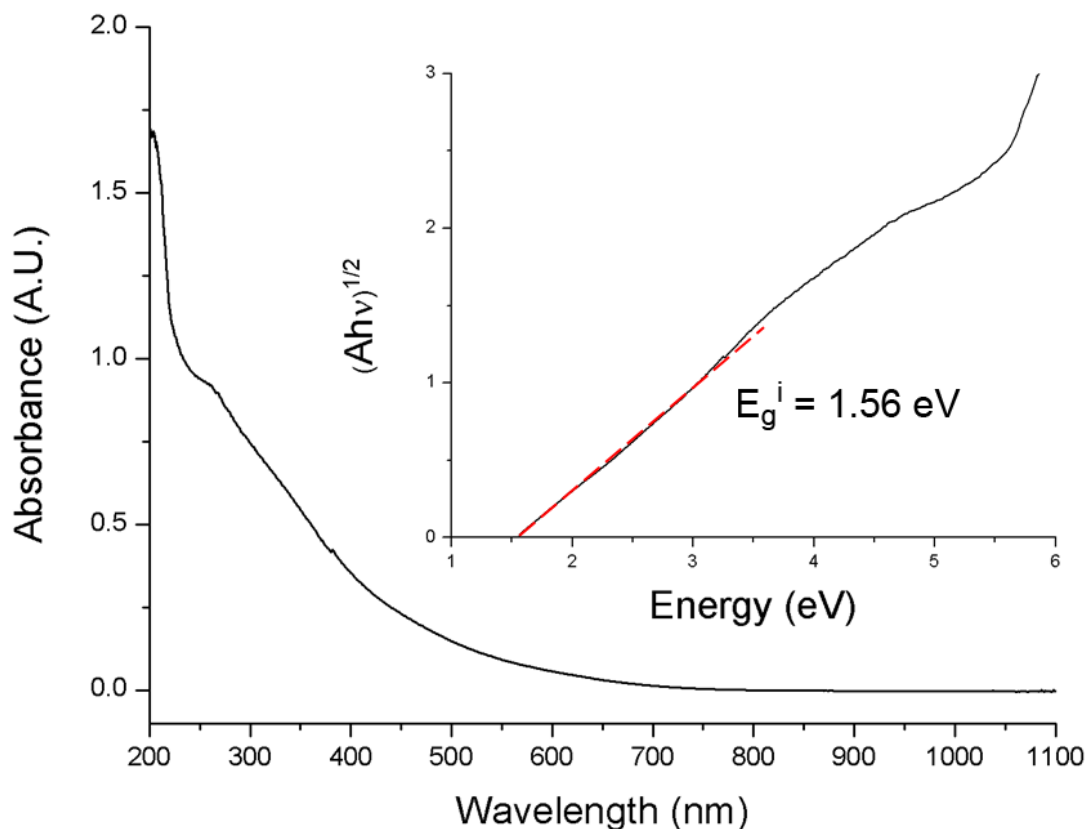


Figure 3.5 UV-Visible spectroscopic results demonstrating optical properties of Cu_3SbSe_3 nanoparticles suspended in hexanes. Inset is the Tauc plot, indicative of an indirect band gap of 1.56 eV.

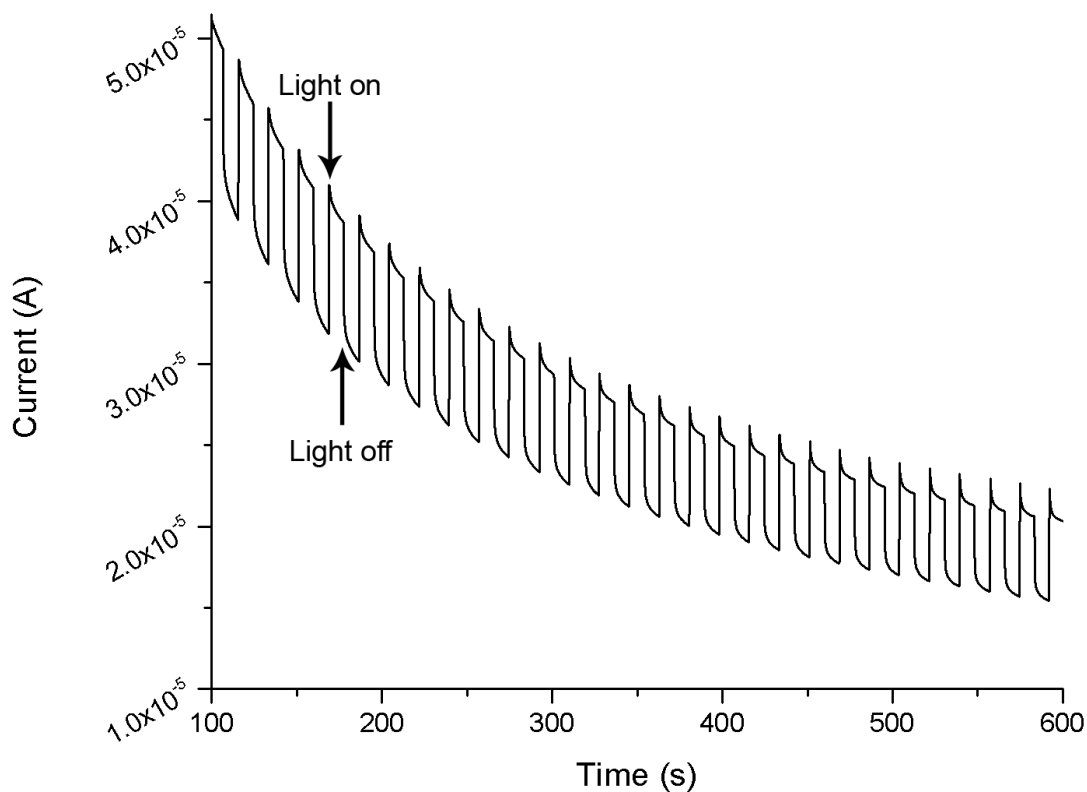


Figure 3.6 Photoelectrochemical measurement of Cu_3SbSe_3 film shows stable p-type photoresponse. Here, the working electrode was a film of Cu_3SbSe_3 ligand-exchanged with TBAI deposited on FTO via dip-coating. The counter electrode used was a platinum basket, in a medium of 0.1 M $\text{Eu}(\text{NO}_3)_3(\text{aq})$ and 0.1 M $\text{KCl}(\text{aq})$. Measurements were performed at -0.2 V vs Ag/AgCl.

In order to assess the electronic properties of these nanocrystals, thin films were dip cast onto a nonconductive substrate. The native ligands were exchanged with Na_2S via a layer-by-layer solid state ligand exchange as described elsewhere.^{23,26} Sodium sulfide exchange provides improved material electronic properties, as measured by the Hall effect. Hall measurements revealed that the Na_2S -exchanged Cu_3SbSe_3 nanodiscs have a conductivity of $1.5 \Omega^{-1}\text{cm}^{-1}$ with a carrier concentration of $2 \times 10^{19} \text{ cm}^{-3}$, which is only slightly larger than those found in other earth-abundant photovoltaic absorber material systems like CZTSe.²⁷

Finally, with the optical and electronic properties characterized and deemed appropriate for photovoltaic applications, photoelectrochemical testing was performed to elucidate how well

these properties couple in the Cu_3SbSe_3 nanodiscs. As shown in figure 3.6, the material exhibits a strong photoactive response, with photocurrents reaching as high as $2.74 \mu\text{A}$ (for a circular area of incident illumination with 0.7 cm diameter). This measured photocurrent is a preliminary result, and optimization of particle size and morphology, film thickness, or ligand exchange could all be used to improve the performance of the material. Also, it should be noted that the photoelectrochemical testing conditions were inefficient, as the film delaminated from the substrate over time resulting in a loss of active material. The dark current also exhibits a decay over time, though both this and film delamination are attributed to the presence of Faradaic current passing at the potential of measurement (as later demonstrated in chapter 5).

3.5 Conclusions

Our work demonstrates a novel synthesis for Cu_3SbSe_3 nanodiscs, and assesses their preliminary optoelectronic properties. It was determined that the disclike morphology is due to dodecanethiol coordination on Se sites of the Cu_3SbSe_3 crystal during growth, preventing growth in the [200] direction. Ligand-exchanged films exhibit acceptable electronic properties for photovoltaic consideration. Despite the indirect band gap determined by optical measurements, the photoactivity observed suggests this material may be an interesting candidate for photovoltaic applications. Further, the results of the photoelectrochemical measurements suggest that sufficient charge can be generated and extracted from Cu_3SbSe_3 to render it a feasible option for future studies to validate the hypothesis that stacking of these nanodiscs may provide enhanced transport properties.

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CHAPTER 4

UNDERSTANDING GROWTH AND STACKING OF Cu_3SbSe_3 NANODISCS[†]

4.1 Introduction

While Cu_3SbSe_3 has been studied theoretically for photovoltaic applications,¹ the optical and electronic properties are less promising than current thin-film materials such as $\text{Cu}(\text{In,Ga})\text{Se}_2$ and CdTe .^{2,3} However, there is a large variability in the results of computational work performed on Cu_3SbSe_3 which suggests the possibility that common computational methods may not be suitable for this material (a common example being the computed band gap ranging from 0.88 eV³ to 1.79 eV¹). Therefore, study of this material retains its importance for both possible photovoltaic application as well as its aid in strengthening theoretical foundations in the search for novel photovoltaic materials.

Experimentally, Cu_3SbSe_3 has been synthesized on the nanoscale and has demonstrated some basic photoactivity.⁴ This method utilizes a dimethylamine borane precursor that is not seen elsewhere in the Cu-Sb-Se system and the work has not been reproduced (though it is necessary to mention that these authors have also reported this precursor in their synthesis of Sb_2Se_3 nanowires⁵ and Bi-Se nanocrystals⁶). Our previous work (chapter 3) reported a separate hot injection synthesis of Cu_3SbSe_3 nanocrystals with a disclike morphology. This nanodisc

[†] This chapter presents the development of a double injection synthesis for Cu_3SbSe_3 . This synthesis improved the ability to explore the morphological controls of Cu_3SbSe_3 nanodisc formation as well as the driving forces governing disc self-assembly.

The synthesis was developed by Daniel Agocs, who also prepared the manuscript with helpful discussions, ideas, and edits by Amy L. Prieto.

morphology is of interest due to the ability of the two-dimensional structures to stack into columns which has also been observed in other systems like Co,⁷ Ni(OH)₂,⁸ In₂S₃,⁹ CuS,^{10,11} Cu₂S,^{10,12} Cu_{2-x}Se,¹³ and CdSe.¹⁴ In this last system, CdSe nanosheets were observed to stack when exposed to antisolvent, and ultralong carrier diffusion lengths were achieved in stacked assemblies.

These ultralong carrier diffusion lengths are of interest as they may provide a method to address arguably the largest problem in nanocrystalline photovoltaics: the large degree of recombination observed as a function of the high density of grain boundaries. Normal nanocrystalline systems exhibit very low power conversion efficiencies without a post-synthetic treatment.¹⁵ Several post-synthetic treatments that have been developed include annealing/sintering deposited films of particles to increase the grain size and ligand exchange to supplant insulating organic ligands at the surface. Instead, we hypothesize that by utilizing the intrinsic ability of these discs to stack into columnar assemblies, we may retain the advantages of solution-processed nanocrystals while minimizing exciton recombination by attaining a large effective crystallite size.

Here, we report a double injection synthesis to assess size and shape control over Cu₃SbSe₃ nanodiscs. The use of diphenyl ether (DPE) is critical to improve disc aspect ratio, and by extension, disc stacking. Though stacks are not long enough to characterize the properties of stacked versus unstacked discs, progress in this direction has been achieved.

4.2 Experimental

Materials and Methods. All chemicals were used as received, and reagent liquids were sparged with N₂ prior to use. Oleylamine (OLA, 70%), copper (II) chloride (CuCl₂ 97%), antimony (III) chloride (SbCl₃ 99+%), and tetrabutylammonium iodide (98%) were purchased

from Sigma-Aldrich. Aniline was obtained from Acros. Se powder (99.99%) was purchased from Strem Chemical. 1-Dodecanethiol (DDT, 98+%) was purchased from Oakwood Chemical. Thiophenol (99+%) was purchased from Alfa Aesar. Sodium hydroxide (98.9%), technical grade acetonitrile, toluene, hexanes (mixture of isomers), methanol, and ethanol (histological grade) were obtained from Fisher Scientific. Reaction vessels were prepared in a N₂ atmosphere glovebox. Reactions were carried out on a N₂ Schlenk line and washing/workup was done on the benchtop.

Double Injection Synthesis. In a typical synthesis, 0.75 mmol CuCl₂ (0.101 g) was mixed with 4 mL OLA in a 25 mL three neck round-bottom flask. Separately, 4 mL DPE was added to a 50 mL three neck round-bottom flask containing 0.33 mmol SbCl₃ (0.75 g). In a 20-mL scintillation vial, 1 mmol Se powder (0.079 g) was dissolved in a combination of 1 mL OLA and 3 mL DDT. Flasks were added to a N₂ Schlenk line using proper airfree technique. The Cu/OLA flask was heated to 110 °C under vacuum and the Sb/DPE flask was held at room temperature under vacuum. Both flasks were allowed one hour to degas while the Se vial was sonicated to ensure complete reduction and dissolution. After the degassing period, both flasks were switched to positive pressure under N₂ and heated to 200 °C. At the reaction temperature, both the room temperature contents of the Se vial and the reactive Cu(OLA) precursor were rapidly and simultaneously injected into the Sb/DPE reaction vessel via gastight Luer-lock syringes. The solution immediately changes to a brown color, indicating nucleation of particles which were allowed 5 minutes to grow. Particle growth was quenched by removal of particles at which time they were washed in a small amount of toluene (<1 mL to prevent solidification) and excess EtOH. The particles were centrifuged at 3500 RPM for 5 minutes. The clear yellow supernatant was decanted and discarded, while the solid particles were redispersed in toluene and flocculated with

EtOH before a second round of centrifugation. The supernatant was again discarded, and the particles were finally suspended in chloroform and centrifuged to separate large agglomerates and poorly capped particles.

Synthesis of Sodium Thiophenylate. Sodium thiophenylate was prepared by facile reaction of sodium hydroxide with thiophenol. Here, 0.302 g sodium hydroxide was dissolved in ~5 mL ethanol, to which 0.77 mL of thiophenol was added. This was stirred for 30 minutes before the temperature was increased to 70 °C to evaporate ethanol. Once the ethanol is evaporated, the sample was dried on a hotplate at 110 °C to ensure removal of ethanol and moisture.

Solid Ligand Exchange. To modify the surface of the nanodiscs, solid-phase ligand exchange was performed. Ligand exchange solutions were made by dissolving 0.2 mmol exchanging ligand in methanol (75 mg tetrabutylammonium iodide in 10 mL methanol). Films were dipped 30 times in the order of: 1. particles suspended in hexanes, 2. exchanging ligand in methanol, 3. acetonitrile (to remove excess ligand). Solutions were unaltered during the dipping process (aside from the addition of solvent to maintain a near constant volume).

Solution Ligand Exchange. To more completely exchange the native ligands on the nanodiscs with thiophenol, a solution-phase ligand exchange was performed. Here, a suspension of the washed nanodiscs in CHCl_3 was added to a separated phase of sodium thiophenylate dissolved in acetonitrile. This mixture was vortexed (30 seconds) and separated by centrifugation (3500 RPM for 5 minutes). The supernatant was decanted and discarded, while the precipitated product was again sonicated and vortexed in acetonitrile. Following centrifugation and removal of supernatant, the resulting particles were dispersed in CHCl_3 though they no longer suspend. For the aniline ligand exchange, the same process was used except 1 mL neat aniline was mixed with

the nanoparticle suspension in chloroform before the precipitation and washing steps were performed using acetonitrile.

Characterization. Powder X-ray diffraction (XRD) analysis was performed on a Bruker D8 Discover X-ray diffractometer using Cu K α radiation ($\lambda=1.54 \text{ \AA}$) and a Lynxeye XE-T position-sensitive detector. Samples were dropcast from chloroform onto a zero background Si sample holder. Transmission electron microscopy (TEM) samples were prepared by dip casting carbon-coated copper grids (200 mesh, Electron Microscopy Sciences) into a particle suspension in hexanes. High-resolution TEM imaging and scanning transmission electron microscopy (STEM)-diffraction was performed on a JEOL JEM-2100F at a working voltage of 200 keV. Low-resolution TEM imaging was performed on a JEOL JEM-1400 at a working voltage of 100 keV. Scanning electron microscopy (SEM) was performed using a JEOL JSM-6500F field emission scanning electron microscope equipped with a Thermo Electron energy dispersive X-ray spectrometer (EDS) operating at 15 keV. FTIR spectra of thin films were obtained with a Nicolet 380 FTIR spectrometer operating in transmission mode. NMR was performed using a Varian 400 MHz spectrometer. UV-Vis absorption measurements were obtained using an Agilent 8453 UV-visible spectroscopy system. Photoelectrochemical testing was performed using a CH Instruments 1230A potentiostat in conjunction with a 65 W Xe arc lamp as a white light source. To simulate the solar spectrum, the lamp beam was filtered using a visible wavelength bandpass filter (Thorlabs, KG3, ~315-710 nm) as well as a 400-nm long-pass filter. The lamp power was adjusted using a ThorLabs S302A thermal power sensor.

4.3 Results and Discussion

In order to effectively encourage stacking of the Cu_3SbSe_3 nanodiscs, understanding the driving forces behind formation of stacks is critical. From a simple model, nanocrystalline surfaces have many sites with unsaturated coordination, resulting in particles with unstable surfaces. Accordingly, to stabilize these high-energy surfaces, discs may assemble into stacks. By extension, if we wish to encourage a large degree of stacking, we must therefore either render individual disc surfaces less stable, or increase the stability of the stacking interaction.

To destabilize individual discs, it is advantageous to increase the area of the unstable disc faces. However, in order to do this, the driving force of disc formation must be understood to achieve morphological control. As established in chapter 3, the disc face is indexed as the (200) plane by HRTEM and STEM-diffraction. This plane is Se-rich, and so our hypothesis is that the dodecanethiol (DDT) may cap on Se sites, preventing growth in the [200] direction while allowing faster growth in all directions perpendicular to the (200) plane, thereby achieving the disclike morphology.

The as-synthesized nanodiscs do exhibit stacking, but typically only to a minor degree. To measure the effect of stacked versus unstacked Cu_3SbSe_3 nanodiscs, it is then important to achieve stacks of a significant number of discs. Therefore, the destabilizing forces must be greater than we have achieved through this synthetic route. If the stacking is observed due to minimization of surface energy, and the disc faces are the stacking planes, then we assume that by exacerbating the surface area of the (200) planes we may encourage a larger degree of nanodisc stacking.

A first pass at increasing the area of the disc faces would suggest growth at a higher temperature so as to grow larger discs. However, a larger disc would increase the surface area of both the unstable disc faces involved in the proposed stacking interaction, but also the otherwise

unimportant disc edges. Therefore, the overall contribution of the disc faces to the total energy of the particle would remain unchanged. Instead, what we actually wish to achieve is to increase the aspect ratio of the discs to increase the percentage of the surface that is the (200) planes. To do this, higher temperatures must be joined with a large degree of (200) surface ligand capping.

It was determined that at temperatures higher than 150 °C, Sb^{3+} reduces in the presence of an electron donating moiety [oleylamine (OLA), dodecylamine, dodecanethiol, 1-octadecene were all explored]. Therefore, the solvent system must be changed in order to perform the synthesis at higher temperatures. Similar to other nanocrystalline systems,^{16,17} diphenyl ether was found to be a useful solvent with a high boiling point of 258.0 °C. Using this small change to the synthesis of Cu_3SbSe_3 nanodiscs, we were able to develop a double-injection synthesis wherein the reaction flask contains SbCl_3 dissolved in diphenyl ether, an injection solution containing CuCl_2 dissolved in OLA, and an injection solution containing Se powder dissolved in a mixture of OLA and DDT; all of which could be prepared separately. These flasks containing SbCl_3 and CuCl_2 were then heated to 200 °C using proper airfree technique, and once equilibrated at temperature the reaction was initialized by the rapid simultaneous injection of Cu/OLA and Se/OLA/DDT into Sb/DPE. After five minutes of growth time, this reaction was quenched by the removal of particles from heat where they could be washed by centrifugation and precipitation before resuspension in chloroform.

As observed by TEM, the resulting discs exhibit a larger aspect ratio than those of the single injection (figure 4.1a). Further, the larger aspect ratio can be initially correlated directly to a larger degree of stacking as seen in figure 4.1. Interestingly, while our original hypothesis involved the surface area of the particles, it can be seen that in order to achieve a larger aspect ratio, the particles are larger and therefore actually possess a smaller surface area-to-volume ratio.

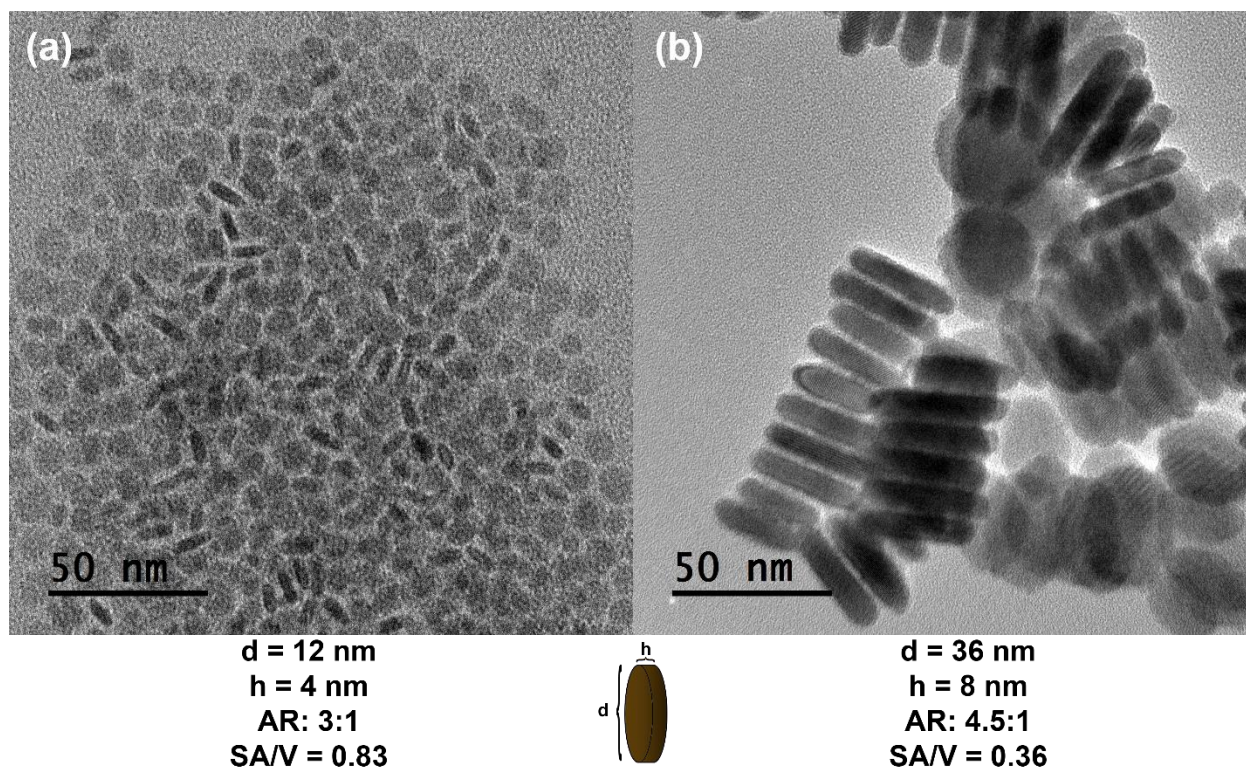


Figure 4.1 High-resolution transmission electron micrographs of (a) single injection and (b) double injection nanodiscs. The discs that result from a single injection are much smaller with an aspect ratio (AR) of 3:1 but a larger surface area:volume (SA/V) ratio of 0.83 whereas the double injection discs have a larger AR of 8:1 but a smaller SA/V of 0.21.

Therefore, it is likely not the surface stabilization alone that can account for the stacking effects observed in these nanodiscs.

Despite the comparison between surface area and volume, the aspect ratio is still important to the stacking behavior. The best stacking has been observed in particles with an intermediate aspect ratio (figure 4.2). Therefore, we may find an optimal value for the size of the (200) face, though at present we do not understand why. A separate rationale for the stacking may also be investigated with respect to not only the discs themselves, but the substrate onto which they are deposited. As these measurements are performed on a TEM grid, it remains to be seen whether the assembly of these nanodiscs into stacks is driven by the deposition procedure onto the grid, or if the stacking is instead driven by self-assembly. To test this, we deposited the nanodiscs onto an aluminum stub for SEM analysis to test if the degree of stacking had any dependency on deposition

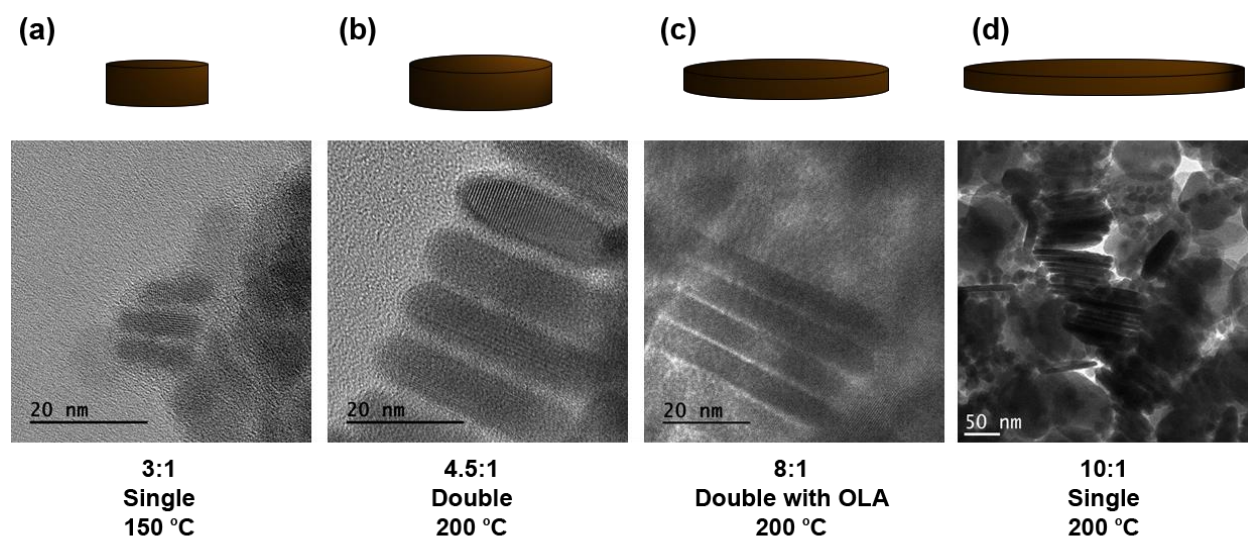


Figure 4.2 Aspect ratio and relative degree of stacking for various selected reaction conditions. Interestingly, larger aspect ratios do not necessarily lead to a larger degree of stacking as sample with a 4.5:1 aspect ratio (figure 4.2) exhibits longer stacks than that with a 8:1 aspect ratio.

procedure. However, the material deteriorated under imaging conditions too fast for micrographs to be obtained. Separate information can be garnered from the preferential orientation of the nanodiscs on a (511)-cut silicon zero-diffraction wafer by X-ray diffraction, though this suggests that the deposition substrate affects only orientation and not necessarily assembly of stacks. To date, an unambiguous alternative to TEM has not proven fruitful to determine the effect of deposition procedure on stacking of the nanodiscs.

The other possibility to drive stacking is to encourage the stability of the stacking interaction. Here, the most straightforward route is the use of an antisolvent. Before understanding solvent interactions with the material, the nanocrystalline surface must first be investigated. As the double injection synthesis uses three possible ligands (OLA, DDT, and DPE), the first step to understanding the surface is to elucidate what ligands are present on the surface. Ideally, in-situ FTIR could be used to observe changes in the stretching modes of the free ligands as binding moieties attach to the surface of the nanocrystals. However, we chose a post-synthetic route to test for the presence of ligands after washing the crystals. This serves two purposes: first, it helps

detail the ligands that are still bound to the surface after washing (though we note that others may play a role in morphology control), and second it helps elucidate the ligands on the surface for subsequent ligand exchange and device fabrication.

After washing the Cu_3SbSe_3 nanodiscs, their compositions were measured by energy-dispersive X-ray spectroscopy (EDS). The EDS spectrum demonstrates the presence of Cu, Sb, Se, C, O, N, and S (supplemental figure S4.1). The Cu, Sb, and Se are all attributed to crystalline constituents, while C is present in all ligands tested. The sulfur is ascribed to DDT, while the N is most likely from OLA. Finally, while oxygen is present in diphenyl ether, the nature of DPE as a noncoordinating solvent and the high oxygen signal relative to sulfur and nitrogen (which coordinate strongly with Cu) suggest that the oxygen signal is likely due to adsorption of oxygen or surface oxidation of the nanodiscs (as seen in other members of the nanocrystalline Cu-Sb-Se family: see chapter 2). To corroborate these results, an FTIR spectrum was obtained for the as-synthesized Cu_3SbSe_3 nanodiscs (supplemental figure S4.2). Unfortunately, M-N and M-S (M = Cu, Sb) stretching modes are difficult to assign, and any ether modes are swamped by other signals such that the presence of DPE cannot be unambiguously disproved. A more thorough characterization may involve ^1H -NMR as observed with ligand stripping on Cu_3SbSe_4 nanocrystals,¹⁸ or through the use of a spatially resolved STEM-EDS line scan to determine the presence of S or N signals at the face (or perpendicular to the face) of the nanodiscs.

Further analysis of the effect of capping ligands during particle synthesis was performed by varying the concentration of the surfactants present during nanodisc nucleation and growth. A series of experiments using large excess of OLA, DDT, and DPE yielded information about particle size and capping. As seen in figure 4.3, the size of the nanocrystals increases from high [DDT] < high [OLA] < high [DPE]. We rationalize that this is likely due to the coordinating nature

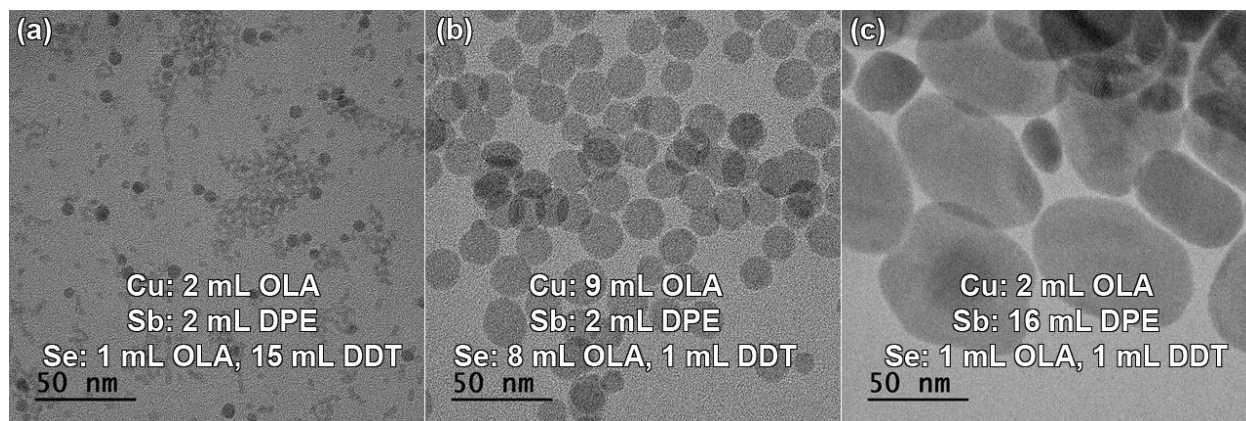


Figure 4.3 TEM images of varied surfactant concentrations. It was determined that a high concentration of DDT (a) yields the smallest particles, while high [OLA] (b) improves monodispersity and suspension and high [DPE] (c) results in unsuspended and polydisperse oblong nanocrystals.

of OLA and DDT, whereas particles grown in excess DPE experience a dilution effect of capping ligands resulting in rapid particle growth following initial nucleation. To the other extreme, high [DDT]-grown particles are the smallest (6.3 ± 0.6 nm) which may be due to the strongly-capping nature of dodecanethiol. However, this reaction also experienced the largest temperature drop which may result in slowing the growth of the Cu_3SbSe_3 nanocrystals. Also of interest in this synthesis is the appearance of a bimodal size distribution of objects present in the TEM micrographs. We attribute the larger crystallites to be Cu_3SbSe_3 whereas the smaller objects are an impurity phase (as observed by the XRD peak at $\sim 46^\circ$ 2θ in figure 4.4, black trace) attributed to decomposition of DDT since a yellow powder (possibly sulfur) was observed on the inside of the flask. Further, the particles formed in the high-[DDT] reaction exhibit preferential growth normal to the (211) plane rather than the (200) plane observed in the normal double injection synthesis (figure 4.4).

The final reaction, high [OLA]-grown particles, exhibits excellent size monodispersity (18.3 ± 2.7 nm). Further, of the three samples the high [OLA] species suspends well whereas high [DPE] does not suspend at all (which may account for the CuSbSe_2 impurity observed in the XRD shown in figure S4.3). The high [DDT] species appears to suspend for a short time (~ 30 minutes),

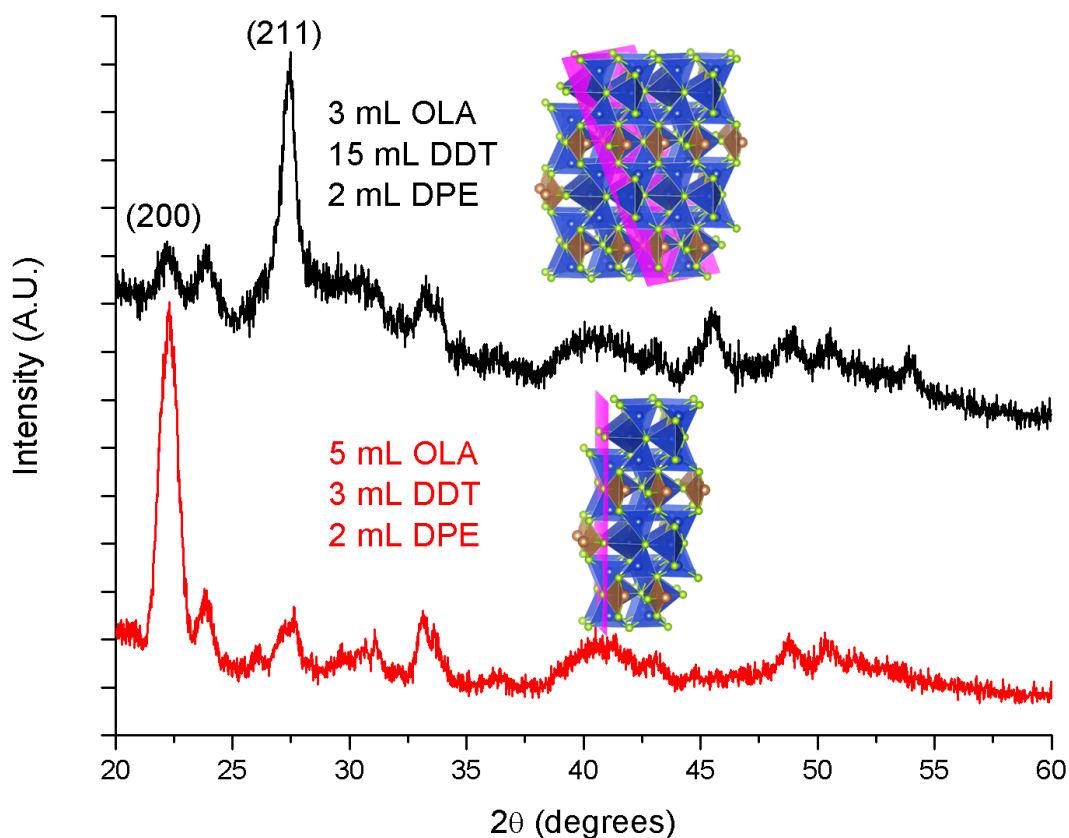


Figure 4.4 XRD patterns of high-[DDT] reaction products (top) and normal growth (bottom) with surfactant volumes given. The relevant lattice planes are shown in pink on the crystal structure correlating to their respective patterns.

though upon shaking the container the particles were revealed to have flaked together and precipitated (which may suggest that the stacking interactions are strong in this sample, and need to be observed over time as the precipitation took ~30 minutes). The suspension is important, as particles resulting from the double injection exhibit poorer suspension (i.e. more dilute suspension) relative to those of the single injection reaction. Also, suspension is critical to the impact of this work as one of the major benefits of the nanocrystalline system is the solution-processability, which is forfeit if the particles do not suspend.

Using this analysis of DDT and OLA likely capping the surface of the discs, we investigated their effect on particle stacking. First, the use of ethanol as an antisolvent during

TEM grid deposition was explored by dipping a grid in Cu_3SbSe_3 /hexanes followed by addition of ethanol to attempt to order the discs. No improvement to stacking was observed in samples to which ethanol was added when compared to samples without antisolvent treatment. Another approach to ligand-involved stacking was taken by attempting to utilize ligand-ligand interactions to crosslink particles.

Initially, a solution-phase ligand exchange was used on washed particles to remove and supplant native ligands with designer ligands as shown in previous work in our group.¹⁵ Using the design criteria of a ligand with two moieties, we chose aniline with a binding amine group similar to OLA and a phenyl ring that was selected for the ability to utilize pi-pi stacking interactions to crosslink particles (figure 4.5). As no improvement to stacking was observed, we rationalized that perhaps the aniline was not binding well to the disc faces, and that instead thiophenol may be a

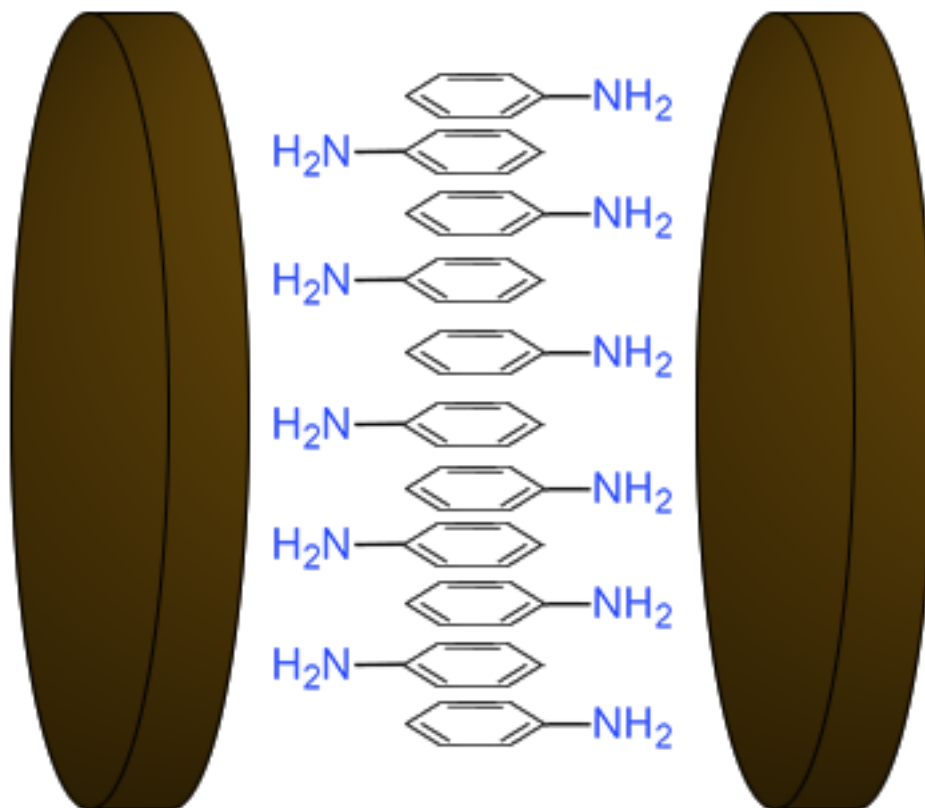


Figure 4.5 Rendition of Cu_3SbSe_3 nanodiscs crosslinked using pi-pi interactions of aniline.

better ligand as it is more akin to DDT and may therefore more adequately bind to the (200) surfaces. As thiophenol and aniline both show an inability to improve stacking, we rationalize that the pi-pi stacking interaction is likely not contributing to stacking due to the relatively similar binding affinities of aniline/OLA and thiophenol/DDT. One final set of experiments was performed using sodium thiophenylate to explore the possibility of an X-type ligand binding more strongly to the disc facets than the neutral L-type thiophenol, though this also failed to lead to an improvement in disc stacking.

A final investigation of the well-stacked nanodiscs reveals that the spacing between individual discs varies. The range of the interdisc spacing is from ~ 1.7 - 2.6 nm. This has some incredible and unforeseen implications for the stacking of these discs. First, the length of a DDT molecule is ~ 0.8 nm. Therefore, ligand interactions are not driving disc stacking (as even assuming there are no interdigitated ligands, two-disc faces should only be ~ 1.6 nm apart at the farthest if ligands are to interact). Further, while the exact distance between nanodiscs may vary based on the focus of the TEM, the variability in the interdisc distance demonstrates that stacking interactions are not conformal. This may suggest that instead of being a crystalline phenomenon, it may instead be something more similar to a coulombic (or zeta potential) phenomenon. For instance, different particles may exhibit different zeta potentials if the surface of these particles is composed of different stoichiometries (though we note this is unlikely due to the homogeneity of the growth solution). Therefore, EDS of individual discs should be measured to identify any variation in composition of disc surfaces.

While we have determined some of the influences of stacking (surface area, particle size, aspect ratio), the difference in synthetic route begets a need for comparison of products of the double injection reaction with the properties of the single injection reaction nanodiscs. If these

materials are to be applied toward photovoltaics, arguably the most important property is their optical absorption in the UV-visible range. As observed in figure 4.6, the absorption properties of resulting particles from both syntheses are similar. The absorption profiles are similar, and Tauc analysis leads to identical band gaps of 1.56 eV. While this gap is indirect in nature, computational studies report a direct gap existing only slightly larger in energy which may enable these particles to still function suitably as photoabsorbers.^{1,2} Further, upon illumination with a light source filtered to roughly resemble the solar spectrum, both single injection and double injection Cu_3SbSe_3 nanodiscs demonstrate a photoresponse (figure 4.7). Chopped light measurements demonstrate the magnitude of photoresponse is small, but significant. Also, the photoresponse of each film is similar, despite the thickness of the two films (the single injection film is thicker by visual inspection). This may suggest that the larger particles resulting from the double injection more efficiently transport photogenerated carriers, possibly owing to the smaller density of recombination sites at grain boundaries.

Despite the small photoresponse exhibited at this juncture, no effort has been made to optimize these films. A simple ligand exchange using tetrabutylammonium iodide is employed due to its success in our lab with a similar system,¹⁵ though other options such as inorganic^{19,20} or

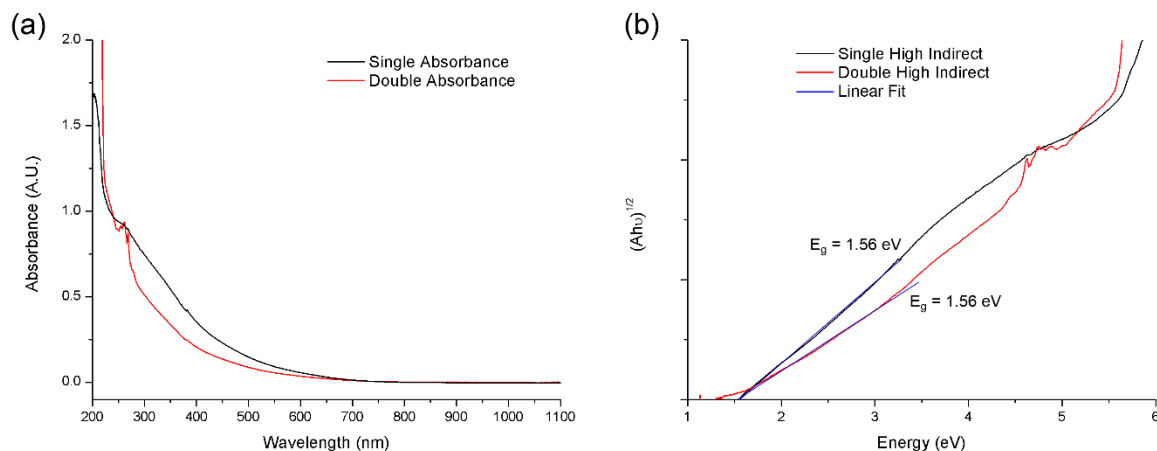


Figure 4.6 Comparison of UV-Vis data for single- and double-injection reactions. (a) UV-Vis absorbance, and (b) Tauc plot for indirect band gaps.

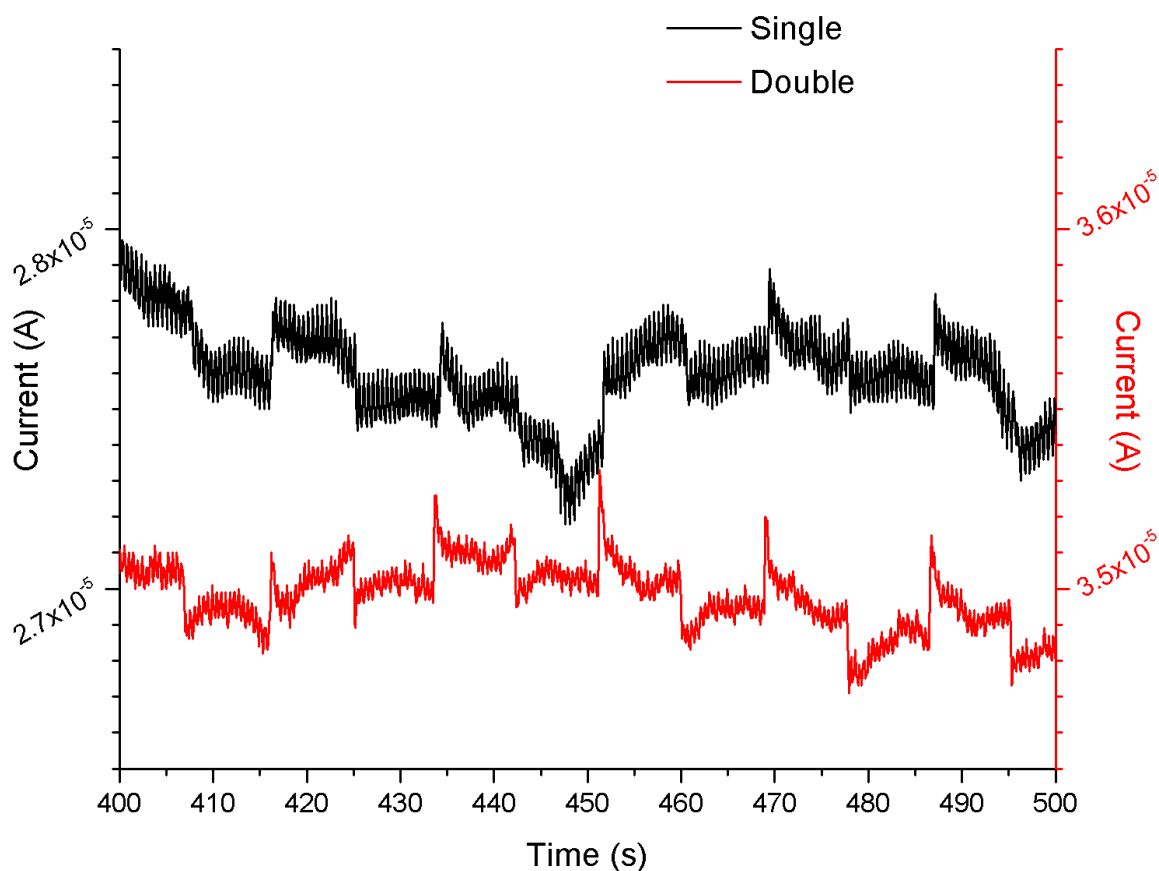


Figure 4.7 Amperometric i-t curves demonstrating photoresponse of single injection and double injection Cu_3SbSe_3 nanodiscs under chopped light irradiation.

conjugated ligands²¹ are likely to better facilitate charge transport through the films. Hall measurements may be useful to elucidate carrier transport within the materials under dark conditions. Further studies are necessary to understand the balance of nanodisc size versus its ability to suspend in solution in order to optimize the photoresponse. The system itself may also be tuned to improve photoresponse characteristics. The identity of the electron scavenger may be selected to encourage electron transfer kinetics (preventing charge accumulation within the film) in conjunction with diffusion considerations. Also, light conditions should be optimized to elicit the maximum photoresponse.

4.4 Conclusions

The double injection reaction for Cu_3SbSe_3 allows higher temperature growth and more control beyond what was established with the single injection system (chapter 3). It was determined that OLA and DDT play a role in particle size, shape, and dispersity. Through manipulation of these properties, the aspect ratio was tuned and a moderate improvement in degree of nanodisc stacking was achieved. Interestingly, the degree of stacking was not observed to be directly proportional to aspect ratio as initially proposed. Despite the modest improvement to stacking, the photoelectrochemical properties of the double-injection-grown particles are comparable to those of the single injection. More work is necessary to improve columnar assembly of the nanodiscs before a benefit can be obtained through stacking.

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CHAPTER 5

ELECTROCHEMICAL METHODS FOR THE ELECTRICAL CHARACTERIZATION OF Cu_3SbSe_3 NANODISCS[†]

5.1 Introduction

While we have reported the single (chapter 3) and double (chapter 4) injection syntheses for Cu_3SbSe_3 , much work remains before this material is understood well enough to be applied efficiently toward full devices. The basic electronic structure of this material has been calculated^{1,2} and explored experimentally^{1,3-5} in the context of thermoelectric applications due to its low lattice thermal conductivity and interesting order/disorder transition.^{6,7} Further, preliminary optical measurements^{8,9} and photoactivity¹⁰ have been characterized. As this material has the potential to be applied toward photovoltaic applications,² a more substantial experimental exploration of the band structure is necessary. This work was initiated by Fernandez et al.⁹ who used Mott-Shottky analysis on thin films of Cu_3SbSe_3 . Their results demonstrate that the flat-band potential changes as a function of pH, indicative of a surface oxide. As our material has nanoscale dimensions, the large surface area may be prone to oxidation^{11,12} which suggests the existence of complicated phase boundaries in this material.

[†] The contents of this dissertation chapter include the electrochemical characterization of Cu_3SbSe_3 nanocrystalline films through cyclic voltammetry and Mott-Schottky analysis which have led to a proposed full cell architecture for a photovoltaic device employing a Cu_3SbSe_3 absorber layer. Additionally, initial results toward understanding phase formation in the copper antimony selenide system are reported.

The measurements, cell design, and manuscript preparation were performed by Daniel B. Agocs. Jeffrey Ma assisted with cyclic voltammetry of SbCl_3 . Amy L. Prieto provided helpful insight, discussion, and editing.

The only material in the Cu-Sb-Se system for which a full photovoltaic device has been fabricated is CuSbSe₂.¹³⁻¹⁷ These devices are based off of previous CuSbS₂ architectures,^{14,18-21} though it is important here to recognize that *all* CuSbCh₂ (Ch = S, Se) device architectures involve a CuSbCh₂/CdS heterojunction, which has been explored and cited as a reason for poor efficiencies due to inefficient band alignment^{13,15,21,22} and light absorption.^{16,20} However, alternative work has suggested that the band offset between CuSbCh₂/CdS is amenable to efficient carrier transport,^{16,23} opening up this subject for further debate. As no comparable heterojunction analysis exists for Cu₃SbS₃, we seek to elucidate the band positions of Cu₃SbSe₃ to determine the identity of efficient heterojunction couples with this material.

Band positions are commonly found using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Mott-Shottky analysis, and photoemission yield spectroscopy (PYS), but examples of this type of analysis have also been conducted using cyclic voltammetry (CV).²⁴⁻²⁸ With this technique, facile measurement can be made for samples deposited on an electrode surface as a thin film. A major pitfall of CV for band position analysis is that many factors can affect the accuracy of the measurement, such as solvent dipoles and overpotentials. However, in order to determine a band alignment the absolute value of the band positions does not need to be known: instead, the values of the band edges must only be elucidated relative to each other. Therefore, by using comparable electrochemistry experimental setups, direct comparison between Cu₃SbSe₃ and a variety of window layer systems may be achieved.

In addition to exploring band alignment for optimizing full device architectures, electrochemical analysis of this system is of interest for investigation of phase formation and *in-situ* analysis of oxidation states. While we have established the three major phases of Cu-Sb-Se materials (CuSbSe₂, Cu₃SbSe₃, and Cu₃SbSe₄) in chapter 1, it is not well understood why a given

synthesis favors one phase over another. As we have described in chapters 2 and 3, injection of the Se precursor into a mixture of CuCl_2 and SbCl_3 can yield either Cu_3SbSe_3 (Sb^{3+}) or Cu_3SbSe_4 (Sb^{5+}). Further, despite the oxidizing nature of the injection reaction, solvated antimony ions can reduce in our synthetic medium if the temperature is raised above 175 °C. To achieve additional control over product phase formation, it is desirable to understand the environment and redox nature of the antimony species in these reactions. We hope to use cyclic voltammetry to determine reduction potentials as a measure of chemical potential in our synthesis medium, and to explore how chemical potentials change throughout our synthesis.

5.2 Experimental

Materials and Methods. Unless otherwise specified, all chemicals were used as received. Oleylamine (OLA, 70%), dodecanethiol (DDT, 98+%), copper (II) chloride (CuCl_2 , 97%), antimony (III) chloride (SbCl_3 , 99+%), ethylenediaminetetraacetic acid disodium salt (EDTA, ~99%), tetrabutylammonium tetrafluoroborate (TBABF_4 , 99%), tetrabutylammonium iodide (TBAI, 98%), hexadecyltrimethylammonium bromide (CTAB, $\geq 98\%$), Cobalt (II) acetate tetrahydrate ($\geq 98.0\%$), ferrocene, and zinc (II) chloride ($\geq 98\%$) were purchased from Sigma-Aldrich. Selenium powder (99.99%) was purchased from Strem Chemical. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na-BARF) was purchased from Boulder Scientific. Tetrabutylammonium chloride (TBACl , $\geq 97\%$) and tetrabutylammonium hexafluorophosphate (TBAPF_6 , $\geq 99.0\%$) were purchased from Fluka. Sodium chloride (NaCl , 99.0%) was purchased from Macron Chemicals. Choline chloride (99.7%) was purchased from VWR. Dichloromethane (DCM, 99.9%) and chloroform (CHCl_3 , ACS grade) were purchased from EMD Millipore. Copper (I) chloride (CuCl) was purchased from Oakwood Chemical. PTFE heat shrink tubing was

purchased from Zeus. 1C Hysol was purchased from Loctite. Conductive Ag epoxy was purchased from Ted Pella. Aluminum (III) chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 99%) was purchased from Alfa Aesar. Sodium dodecyl sulfate (SDS) was purchased from Pfaltz & Bauer. Carbon foam was purchased from ERG Materials and Aerospace. Technical grade toluene, acetonitrile, hexanes (mixture of isomers), methanol, histological grade ethanol, ethylene glycol, and sodium sulfate were purchased from Fisher Scientific. Ethaline was prepared by heating a 2:1 (wt/wt) choline chloride:ethylene glycol mixture to 70 °C while stirring. Oleylamine and dodecanethiol were sparged for 2 hours with nitrogen to degas prior to first use.

Cu_3SbSe_3 Synthesis and Ligand Exchange. To synthesize Cu_3SbSe_3 , the single injection route detailed in Chapter 3 was employed. Upon suspension in hexanes, a solid-phase ligand exchange (detailed in Chapter 2) was used wherein 20 mM TBAI was dissolved in methanol as an exchanging solution to deposit thin films of Cu_3SbSe_3 on FTO.

Carbon Foam Counter Electrode Fabrication. To prepare carbon foam counter electrodes, PTFE heat-shrink tubing was recovered at 340 °C for 15 minutes around a straightened stainless steel wire. The wire was then contacted to a 0.5 mm x 0.5 mm carbon foam. This contact was adhered using silver epoxy (cured one day on the benchtop), and the epoxy was chemically protected using Hysol, which was allowed to cure for 3 days before use.

Electrochemical Experiments. For all cyclic voltammetry measurements described here, a CH Instruments 1230A potentiostat was used. Cyclic voltammetry measurements obtained in acetonitrile were performed using a glassy carbon working electrode (3 mm diameter), Pt basket counter electrode, and Ag/AgCl reference electrode. The supporting electrolyte was 0.1 M TBAPF₆ and the scan rate was set to 50 mVs⁻¹. For experiments measuring a Cu_3SbSe_3 film, the film was deposited directly onto the glassy carbon working electrode surface from a suspension in

CHCl₃, where the film was allowed to dry in air before measurement. For a typical cyclic voltammetry measurement obtained in oleylamine, a glassy carbon working electrode, carbon foam counter electrode, and Ag/Ag⁺ reference electrode were used. This configuration was varied as described in the text. For cyclic voltammetry measurements obtained in dichloromethane, a glassy carbon working electrode, Pt basket counter electrode, and Ag/AgCl reference electrode were used in conjunction with 0.1 M TBABF₄ supporting electrolyte.

Mott-Schottky Analysis. Flat-band measurements were performed using a CH Instruments 660C potentiostat. The working electrode was prepared by dipping a film of Cu₃SbSe₃ onto a FTO-glass substrate. The counter electrode was a Pt basket, and the reference electrode was Ag/AgCl. Supporting electrolyte was 0.5 M sodium sulfate in deionized water. Measurements were performed over a range of -0.2 V – 1 V with a 1 kHz frequency.

5.3 Results and Discussion

To measure the band positions of Cu₃SbSe₃, we adopted a method reported in literature for similar complex copper chalcogenides.^{29,30} In this system, we used a three-electrode cell where the working electrode was a thin film of Cu₃SbSe₃ drop cast onto a glassy carbon surface from a suspension in chloroform. Figure 5.1 shows the difference between cyclic voltammograms obtained from the neat electrode surface (clean glassy carbon) and the electrode functionalized with Cu₃SbSe₃ nanodiscs. While the reversible process at -0.92 V vs Ag/AgCl is attributed to exposure to air (Supplemental Figure S5.1), several features appear only with the presence of the Cu₃SbSe₃ film. The small current observed at oxidizing potentials (>1 V vs Ag/AgCl) is assigned to solvent breakdown. This process is not fully reversible due to the diffusion of these species away from the electrode surface. At more negative potentials, we observe a Faradaic current onset

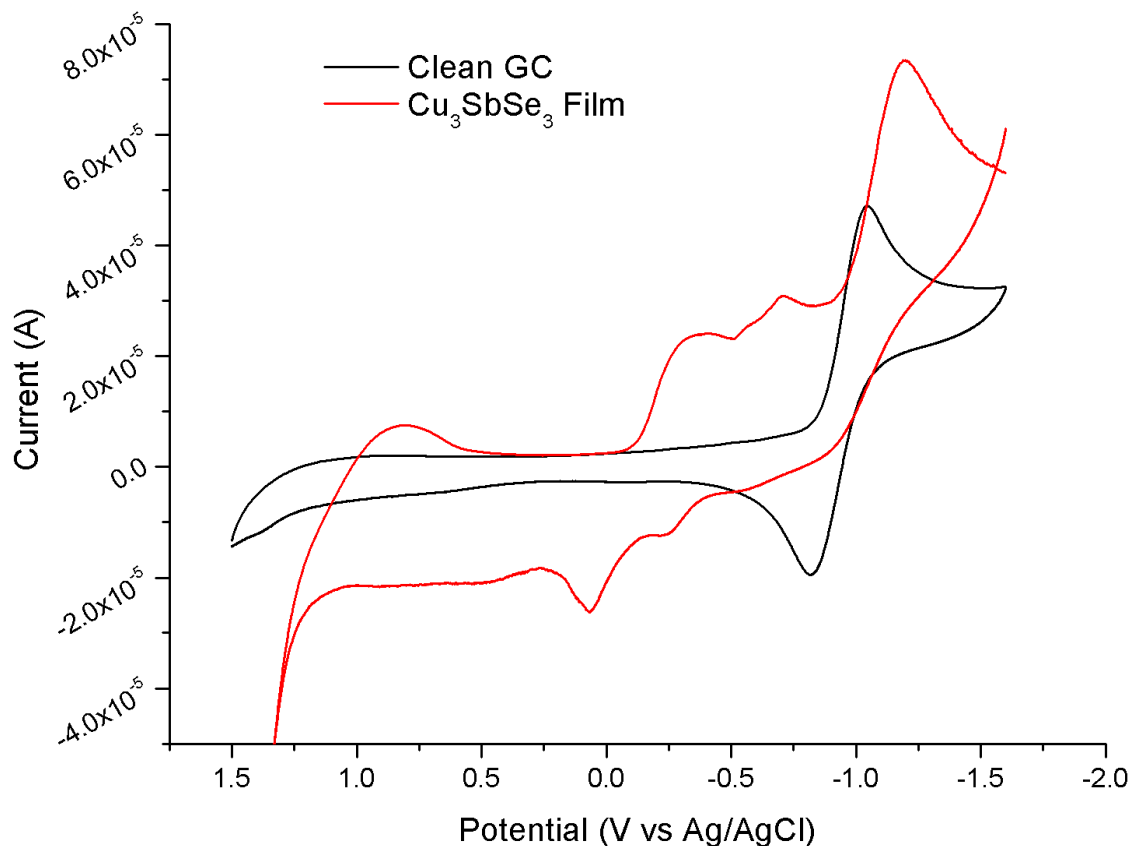


Figure 5.1 Cyclic voltammograms of clean glassy carbon working electrode surface (black) and the same electrode functionalized with a thin Cu_3SbSe_3 nanodisc film (red). Both measurements were obtained in acetonitrile with a scan rate of 50 mV/s using a solution of 0.1 M TBABF₄. The onset of cathodic peaks at 0.1 V vs. Ag/AgCl demonstrates the reduction of the conduction band.

at 0.12 V which we assign to reduction of the conduction band minimum (CBM). Converting this to the vacuum level (Supplemental Figure S5.2), we have determined the CBM position of Cu_3SbSe_3 to be -4.62 eV. Using the previously obtained optical band gap for Cu_3SbSe_3 (Figure 4.3b) of 1.56 eV, we assign the valence band maximum to -6.18 eV.

These values for the band edge positions are significantly different than those for other Cu-Sb-Ch (Ch = S, Se) species, leading to the conclusion that cyclic voltammetry experiments may be convoluted by competing surface phenomena such as dipole rearrangement or formation of an electrical double layer. Therefore, we also measured the flat-band potential of Cu_3SbSe_3 to isolate the position of the valence band maximum without surface interactions (Figure 5.2). This Mott-

Schottky analysis was performed using a film of Cu_3SbSe_3 deposited onto an FTO substrate via solid-phase ligand exchange using tetrabutylammonium iodide. The x-intercept of the linear region yields the flatband potential of the Cu_3SbSe_3 to be at -5.27 eV, and the corresponding valence band maximum to be at -5.33 eV. Therefore, the band edges (VBM = -5.33 eV, CBM = -3.77 eV) are suitable for heterojunction with CdS. To promote efficient carrier transport throughout a device using well-investigated materials, we proposed that a substrate cell architecture of FTO/ Cu_3SbSe_3 /CdS/Al should be feasible with a maximum open circuit potential of ~770 mV. We do note that as the Fermi energies align in this heterojunction, the bands will bend in Cu_3SbSe_3 and CdS suggesting that this junction may not be efficient and further work will

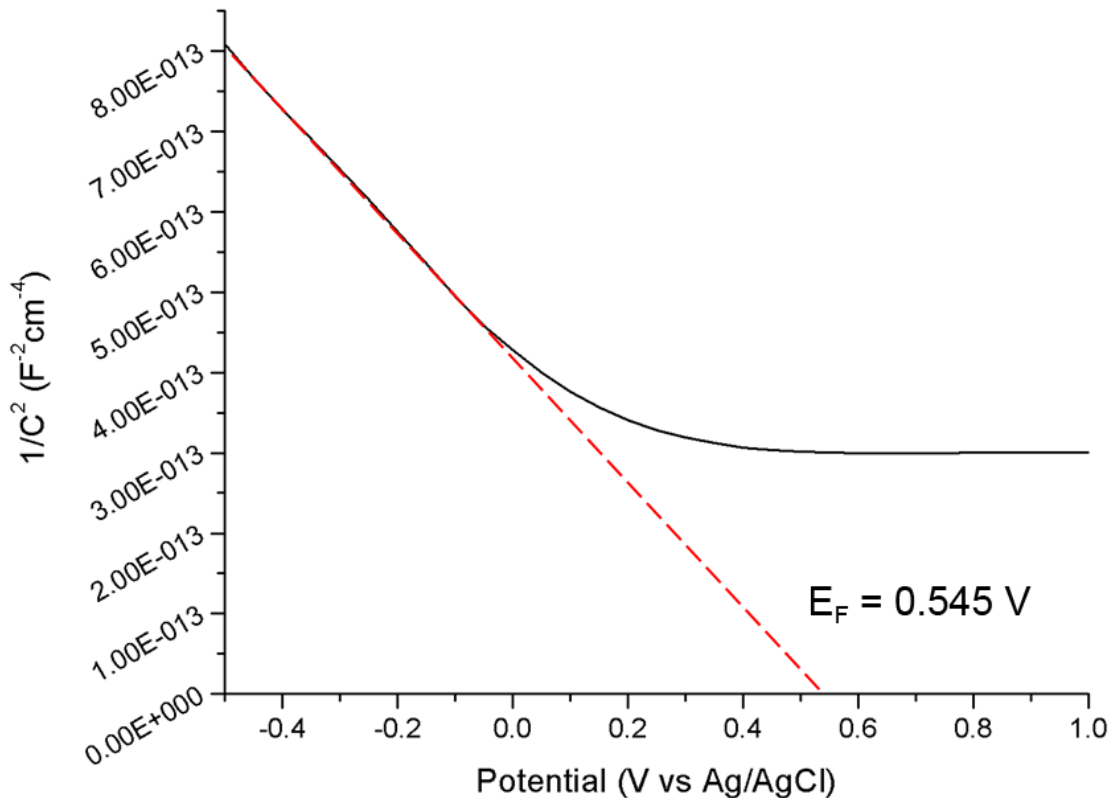


Figure 5.2 Mott-Schottky analysis of Cu_3SbSe_3 film deposited on FTO via solid ligand exchange using tetrabutylammonium iodide. Extrapolating the linear portion of the data to the x-axis yields the $E_F = 0.545 \text{ V}$ vs Ag/AgCl, or -0.527 V vs vacuum. The negative slope of the linear portion supports the p-type character in the film.

be necessary, though we propose this cell architecture as a starting point for device analysis for architectures including a Cu_3SbSe_3 -absorber layer.

As expected, the conduction band position of Cu_3SbSe_3 by Mott-Schottky analysis is close to the value reported for the similar compound CuSbSe_2 (-3.84 eV).¹⁶ However, this value is still significantly more positive than other complex copper-chalcogenide materials like $\text{Cu}_2\text{ZnSnSe}_4$ (-4.33 eV)^{22,31} or $\text{Cu}(\text{In,Ga})\text{Se}_2$ (-4.3 eV).²² Therefore, common n-type layers including CdS may not be as desirable as initial analysis may suggest. Instead, if the degree of band bending is significant it may be agreeable to use an n-type layer with a higher CBM such as ZnS (CBM = -3.46 eV)³² or suitably doped CdS to account for or adjust the degree of bending.

Aside from using electrochemical methods to better characterize the material, we are also interested in using observed reduction potentials to model the chemical potentials of species in solution to improve our understanding of synthetic conditions. In order to obtain useful information about synthetic conditions, it is necessary to develop a system capable of performing electrochemical measurements in the reaction medium, at operating temperature and while maintaining an air-free environment. As the bulk of this synthesis is performed in oleylamine, we must establish a system with which to perform electrochemical measurements in this medium.

To the best of our knowledge, there do not exist any reports of electrochemical measurements performed in oleylamine. Therefore, for preliminary measurements we chose to assess alternative electrode architectures in place of traditional electrodes. In this setup, both our working and counter electrodes were stainless steel wires, with a Ag/AgCl reference electrode (Figure 5.3). It should be noted that AgCl immediately dissolved in oleylamine, leaving our reference electrode as the Ag/Ag^+ couple. As this couple is not buffered, it is an inappropriate reference electrode for quantitative measurements, though it completes the cell such that we may

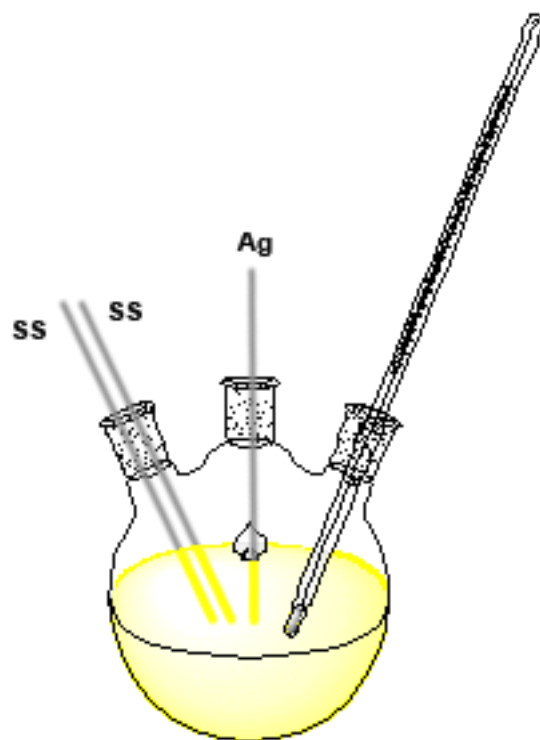


Figure 5.3 Depiction of initial electrochemical cell for cyclic voltammetry in oleylamine. The working electrode is stainless steel (SS), the counter electrode is SS, and the reference electrode is a silver wire. The third neck of the flask is a thermocouple for monitoring temperature.

observe any reversible electrochemistry that occurs. No supporting electrolyte was used, as the concentration of precursor salts (analyte) used was comparable to traditional supporting electrolyte concentrations (on the order of 0.1 M). Most common supporting electrolyte salts for organic media were determined to be insoluble in oleylamine. Interestingly, our initial assumption that the reagent salts would render a conductive solution was false, as CuCl_2 dissolved in oleylamine yields a blue solution indicative of Cu^{2+} , though the solution was too resistive to register a measurement when analyzed using a multimeter. Similarly, SbCl_3 was observed to dissolve into oleylamine, though only at temperatures above its melting point (73.4 °C), and the resulting solution also resisted passing any current. As a solution of CuCl_2 and SbCl_3 alone is insufficient to yield an appropriate electrochemical measurement solution, additional supporting electrolytes were investigated (Table 5.1). When investigating common supporting electrolyte salts for organic

media, most were determined to be insoluble in oleylamine. To this end, it was determined that sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Na-BARF) readily dissolves in oleylamine and produces a conductive solution (though possible issues are noted with formation of insoluble NaCl in mixtures of Na-BARF with CuCl_2 and/or SbCl_3).

With a viable solution established, cyclic voltammetry (CV) measurements were obtained, though reversible electrochemical behavior was not observed. No Faradaic signal was found for any of the analyte species we attempted to measure, leading to the conclusion that our electrode surface may not be amenable to fast electron kinetics or sufficient charge transfer. To test this, the stainless steel working electrode was used in a more ideal cell (0.1 M TBABF₄, 0.001 M ferrocene in acetonitrile), with a platinum basket counter electrode and a saturated calomel reference electrode. The results (Figure 5.4) demonstrate that no Faradaic current was observed using the stainless steel working electrode, suggesting it is not an acceptable electrode. Instead, glassy carbon was utilized for future experiments as this electrode was capable of measuring the expected CV for the ideal acetonitrile solution. However, initial measurements in oleylamine using the

Table 5.1 Solubility of supporting electrolyte species in oleylamine.

Species	Solubility Conditions
Tetrabutylammonium chloride (TBACl)	Insoluble
Sodium dodecyl sulfate (SDS)	Insoluble
Ethylenediaminetetraacetic acid (disodium salt, EDTA)	Insoluble
Tetrabutylammonium tetrafluoroborate (TBABF ₄)	Insoluble
Tetrabutylammonium iodide (TBAI)	Insoluble
Tetrabutylammonium hexafluorophosphate (TBAPF ₆)	Insoluble
Cetrimonium bromide (CTAB)	Insoluble
Sodium chloride (NaCl)	Insoluble
Zinc (II) chloride (ZnCl_2)	Insoluble
Aluminum (III) chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$)	Insoluble
Antimony trichloride (SbCl_3)	Soluble above 73.4 °C (melting point)
Cobalt (II) acetate tetrahydrate [$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$]	Soluble at room temperature, but solution is resistive suggesting complexation
Copper (I) chloride (CuCl)	Soluble at room temperature, but solution is resistive suggesting complexation
Copper (II) chloride (CuCl_2)	Soluble at room temperature, but solution is resistive suggesting complexation
Sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Na-BARF)	Soluble, conductive solution

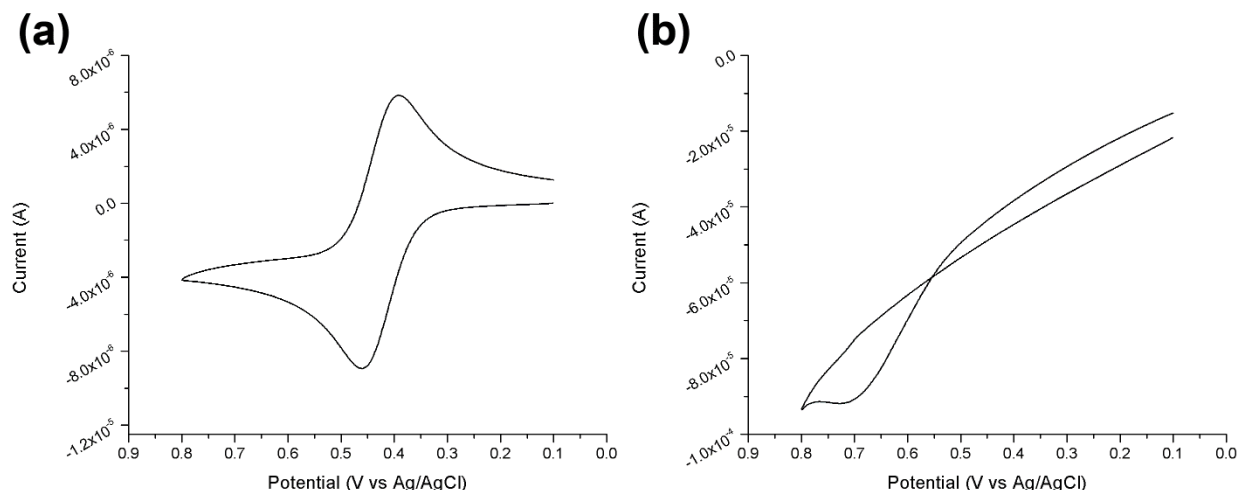


Figure 5.4 Cyclic voltammograms of ferrocene on (a) a retail Pt working electrode, and (b) a stainless steel wire working electrode. No Faradaic current was observed with the stainless steel electrode.

glassy carbon working electrode still do not yield any signal which suggests the oleylamine may be fouling the electrode surface.

To assess the interaction of oleylamine with the glassy carbon working electrode surface, measurements were performed using SbCl_3 in an innocent solvent. Due to its large electrochemical window, dichloromethane (DCM) was chosen, and cyclic voltammograms were obtained (black trace in Figure 5.5). Two primary peaks were observed within the electrochemical window, with reduction of Sb^{3+} to Sb^0 at -0.4 V vs Ag/AgCl and subsequent stripping of Sb^0 observed with an onset of oxidation at ~ 0 V vs Ag/AgCl. Interestingly, the oxidation of $\text{Sb}^{3+/5+}$ may be visible at ~ 0.7 V vs Ag/AgCl, though the signal observed is far less than the $\text{Sb}^{3+/0}$ couple. Next, the same CV was measured, though with small amounts of oleylamine added to solution (Figure 5.5). Upon addition of oleylamine, the electrochemical behavior of Sb is significantly altered. With a small amount of OLA (0.18 mL, 1.8 vol %), the overpotential required for the three-electrode reduction of Sb^{3+} to Sb^0 is increased such that the peak in the cyclic voltammogram is greatly shifted, requiring sufficient overpotential that the corresponding peak may appear more negative of solvent reduction. Evidence of this reduction is present by the subsequent oxidation and stripping of Sb^0

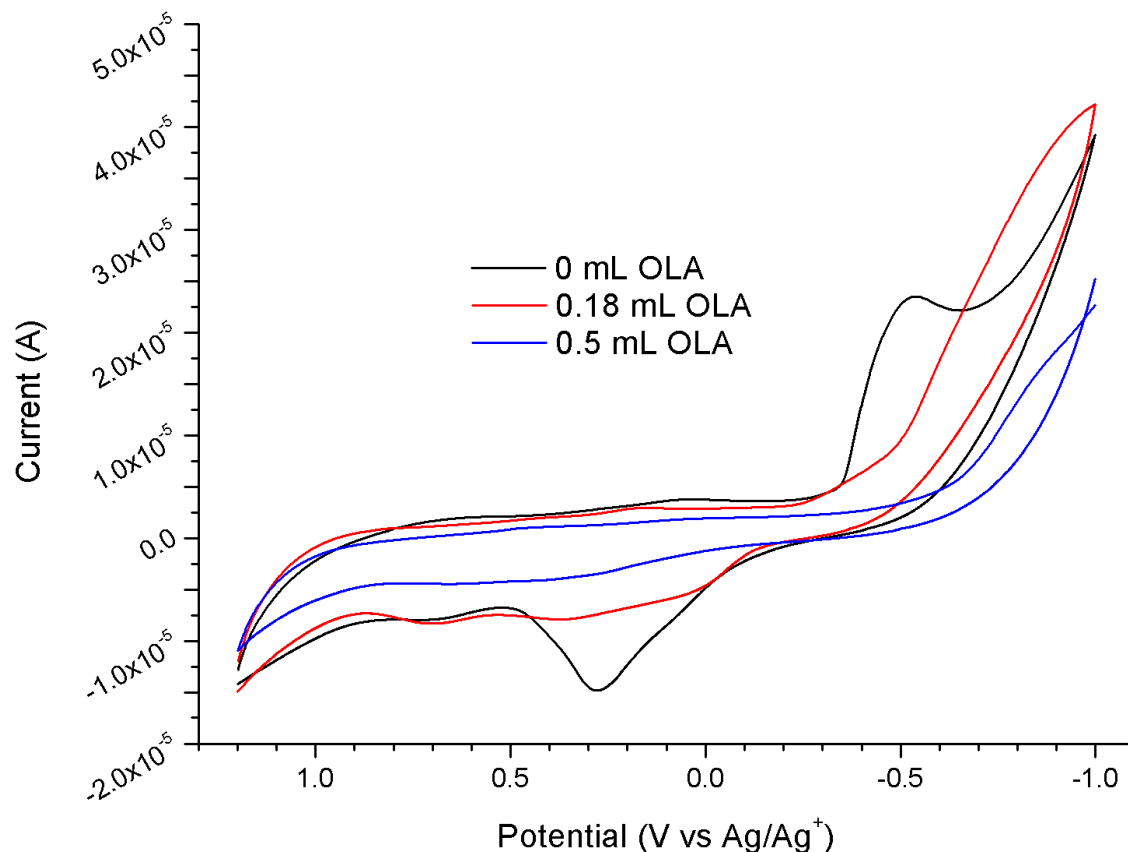


Figure 5.5 Cyclic voltammograms of SbCl_3 in DCM with varying amounts of OLA added. The reduction of Sb^{3+} to Sb^0 is significantly limited in the presence of any oleylamine, while the current due to stripping of Sb^0 is limited in the presence of a small amount of OLA. When the concentration of oleylamine is increased, there is almost no signal observed for Sb^0 stripping and the onset is at a more positive overpotential.

from the electrode surface during the reverse scan. However, if the amount of oleylamine is further increased to 0.5 mL (4.8 vol %), the Sb^0 stripping peak changes drastically, with a much lower peak current and a much larger overpotential before the onset of stripping is observed (Figure 5.5, blue trace). These combined effects strongly suggest interaction of oleylamine with the electrode surface, with the amine likely fouling the working electrode. Upon addition of any oleylamine, peaks attributed to reduction and oxidation of SbCl_3 are greatly suppressed, indicating the fouling of the electrode surface by the presence of oleylamine. While the exact cause for this is currently

unknown, there are literature reports of interaction between oxidized amines and glassy carbon working electrode surfaces.³³⁻³⁵

Another noteworthy experiment was performed using ethaline instead of DCM. While the peaks for Sb^{3+} reduction and Sb^0 oxidation are more well-defined in ethaline than DCM, the use of ethaline also clearly elucidates the position of the $\text{Sb}^{5+/3+}$ couple at ~ 0.8 V vs Ag/AgCl (Figure 5.6, bottom). This couple is critical to understanding the copper-antimony-selenide system as finely tuning synthetic parameters can yield Cu_3SbSe_3 (Sb^{3+}) or Cu_3SbSe_4 (Sb^{5+}) phases.

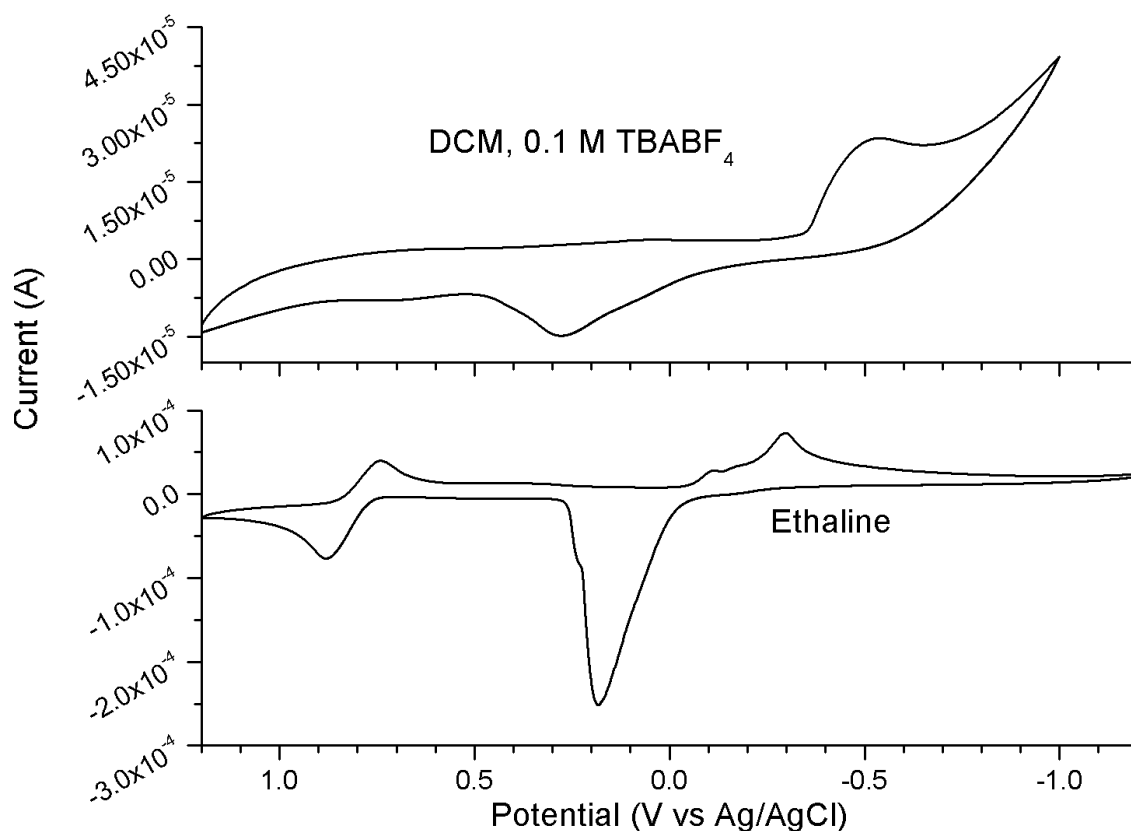


Figure 5.6. Cyclic voltammograms of 1 mM SbCl_3 in (a,b) DCM and (c) ethaline. The presence of a reversible peak at ~ 0.8 V vs Ag/AgCl is only observed in the ethaline trace. In all cases, a glassy carbon working electrode (3 mm diameter) was used with a platinum basket counter electrode and Ag/AgCl reference electrode. For DCM samples, 0.1 M TBABF_4 was used as a supporting electrolyte.

5.4 Conclusions

Initial measurements of the electronic structure of Cu_3SbSe_3 using Mott-Schottky analysis have been successful in locating the position of the valence band. This value is attributed to -5.33 eV, which was then used in conjunction with the optical band gap (determined in chapter 3) to yield a conduction band position of -3.77 eV. These results lead to identification of several possible n-type heterojunction material matches for Cu_3SbSe_3 . In conjunction with the established photoactivity of this material (chapter 4), these allow for development of a full photovoltaic cell. We propose a substrate architecture of FTO/ Cu_3SbSe_3 /CdS/Al to begin analysis of cell function.

Aside from measurements of the synthesized products, cyclic voltammetry was also attempted to understand the synthetic processes resulting in the formation of these nanodiscs. Though no CV has been obtained in a system containing oleylamine, much of the preliminary groundwork has been laid to understand and potentially overcome the challenges present in obtaining this measurement. Looking forward, ethaline appears to be an excellent solvent to understand the shifts in redox behavior of Sb as both the $\text{Sb}^{5+/3+}$ and $\text{Sb}^{3+/0}$ couples are readily observable. Further, as oleylamine has been observed to foul the surface of all electrodes tested, pursuit of a hanging mercury drop electrode may allow us to take advantage of a constantly fresh electrode surface in order to obtain measurements in this medium. This may make it possible to electrochemically measure various species to directly observe their interactions, allowing us to discern conclusions about how the mechanisms proceed which is sorely lacking in the field of nanocrystalline synthesis. Electrochemical measurement in the presence of amine surfactants would contribute in the broader context of aiding our understanding of not only synthetic mechanisms but may also help to open up electrodeposition and electrochemical measurement as viable avenues to investigate these nanomaterials *in-situ*.

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CHAPTER 6

SUMMARY OF THIS RESEARCH AND RECOMMENDATIONS FOR FUTURE DIRECTION

There have been many significant improvements recently in the field of energy generation and conversion, though the global energy supply is still dominated by coal and natural gas. These sources produce greenhouse gases which has led to rising concerns over climate change and have led to a push toward alternative renewable energy methods. Despite the surge in interest, renewable technologies only account for a small portion of the market share of energy production, with a need for further research to improve these sources and drive down the cost.

Among these renewable technologies, wind energy has been the frontrunner. However, complaints against wind power include the inconsistency of weather, noise from the turbines, and visual pollution. Other renewable technologies include hydroelectric, solar, and geothermal power. While opponents of hydroelectricity argue about the effect of reservoirs on the environment and inefficacy during droughts, photovoltaic and thermoelectric sources tap the potential of energy provided by the sun and waste heat (respectively) in a quiet, abundant, and minimally invasive way.

Thermoelectricity can assist in energy generation and loss minimization, especially in improving industrial use of waste heat and energy use efficiency. Currently, thermoelectric materials are utilized in specialized applications (such as extraterrestrial power generation) due to their lack of moving parts and robustness towards mechanical failure. However, these materials are not yet commercially viable due largely to their low efficiencies, though the concept of low-

dimensionality has spurred a resurgence of research in this field since the turn of the 21st century. Further, as phonon scattering is desirable in thermoelectric materials, they are often composed of large, polarizable or “soft” elements such as lead or tellurium that are environmentally harmful or rare. These adverse factors can contribute to increasing manufacture cost and further delay commercialization of thermoelectric generators. This has translated to a small area of the field turning to investigation of earth-abundant thermoelectricity. Though some earth-abundant materials have been investigated for their thermoelectric function, the achieved figures of merit are considerably low even when compared to high-efficiency materials (which are still inadequate for commercial application). Here, the Cu-Sb-Se system is very promising as both Cu_3SbSe_3 and Cu_3SbSe_4 exhibit minimal thermal conductivity values, and of these Cu_3SbSe_4 demonstrates promising electronic conductivity.

There has been a significant amount of research performed on Cu_3SbSe_4 as explained in chapter 1. This has primarily focused on doping effects and nanoscaling of the material. However, in nanomaterials there is a large surface area-to-volume ratio, which must be taken into consideration for device function. In chapter 2, we investigated Cu_3SbSe_4 nanocrystals electronically under ambient conditions and observed that the surface oxidizes in air. This surface oxidation leads to an improvement in electronic conductivity, likely due to an increase in hole mobility throughout the film. The hole mobility increase was linked to oxidation of all constituent elements via XPS (in the form of Cu^{2+} , SeO_2 , and an Sb-O binding environment). This exploration of the oxidation in Cu_3SbSe_4 nanocrystals and the subsequent correlation to electronic properties may help elucidate surface treatments in this material to contribute to further optimization of a system that has demonstrated an excellent thermoelectric figure of merit for an earth-abundant material.

Apart from thermoelectricity, solar absorption is another renewable energy source. Photovoltaics, when paired with adequate energy storage, has the potential to provide more energy than humans currently consume. Further, as the population grows, solar energy is a promising avenue to improve the energy supply. The major detractions of implementing solar energy are the high cost per watt and the exotic materials in use. To this end, there is a broad search for novel high-efficiency earth-abundant photovoltaic materials. While $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ is the leader for earth-abundant photovoltaics, its power conversion efficiency has been limited to 12.6% by low open-circuit potentials, often cited to be due to cation disorder. An alternative system that has been garnering interest is the copper antimony chalcogenide family. While there is a broader body of literature surrounding the Cu-Sb-S materials (likely due to the comparative ease of synthesis), theoretical predictions suggest Cu-Sb-Se materials may be more efficient for solar energy harvesting.

Though CuSbSe_2 has the largest potential for a high power conversion efficiency, it has been synthesized and incorporated into full devices to the point where the next step in optimization will be a greater understanding of the underlying physics of cell performance. However, Cu_3SbSe_3 also has a band gap amenable to solar spectrum absorption and has gone relatively unnoticed for photovoltaic applications. In chapter 3, we have dictated a hot injection synthesis of Cu_3SbSe_3 nanodiscs, and their preliminary optoelectronic properties. They demonstrate absorption of the solar spectrum and exhibit small photocurrents upon illumination. Further, these nanodiscs possess an interesting morphology that we believe may be used to address one of the major issues within nanocrystalline photovoltaics, namely the large density of grain boundaries. We investigated our synthesis more thoroughly and developed the double injection synthesis reported in chapter 4. Despite demonstrating control over particle size and aspect ratio, the optoelectronic

properties of the films do not change significantly, with both films exhibiting similar absorption spectra and photoactivity, though the double injection particles may be more efficient as thinner films were able to generate similar photocurrents.

Through our synthesis development, we determined that the product phase formation is subtle, and is affected by a variety of factors. Stoichiometry affects phase formation, as was rationally expected, though excess antimony is necessary to form phase-pure Cu_3SbSe_3 . Aside from stoichiometry, we also explored the effect of thiols present during the synthesis. We determined that the identity of the thiol affects whether the predominant phase is Cu_3SbSe_3 or Cu_3SbSe_4 . To better understand the phase formation in this system, we attempted a series of electrochemical measurements in chapter 5. The major challenge of these measurements is overcoming the fouling of the electrode surface by oleylamine, but if this can be circumvented, the ability to measure redox potentials for this type of synthesis *in situ* has significant ramifications toward a stronger mechanistic knowledge of solution-phase nanocrystalline synthesis.

Another reason to support electrochemically measuring the redox potentials in this synthesis stems from the product formation. Though Cu_3SbSe_3 can be formed in the absence of thiol, the thiol was determined to be critical for achieving a nanodisc morphology. This morphology is exciting, especially as the discs self-assemble into columnar arrangements. We have hypothesized that this is a stabilizing effect wherein the discs minimize their interfacial energy. This stacking could improve electronic transport by achieving a larger effective crystallite size while retaining the ability to solution process this material. To understand the driving forces behind the stacking, we investigated the disc formation and discovered that the nanodiscs cap on the (200) faces, which is due to thiol capping of the surface. Interestingly, we were able to tune the surface-to-volume ratio using the particle size and temperature of growth and found that the

assembly is not a function of this ratio as we had hypothesized. Further, the interparticle spacing is not perfectly regular, which implies that the assembly is not a ligand-driven effect. Additional work to understand and extend the degree of stacking is a promising avenue, as this has not been elucidated for complex multinary nanostructures and may have strong implications for carrier transport in these materials.

Apart from the stacking, the Cu_3SbSe_3 exhibited exciting optoelectronic properties. Thin films of the particles demonstrate solar spectrum absorption, with an indirect band gap of ~ 1.5 eV. While the indirect band gap is not ideal, the material still exhibits strong absorption and photocurrents have been measured, indicating the ability to extract photoexcited carriers from the film. Therefore, it is desirable to determine an appropriate n-type material to fabricate a p-n heterojunction and develop a full cell.

To this end, we utilized electrochemical measurements to investigate material properties (chapter 5). The conduction band minimum was obtained via cyclic voltammetry, and in conjunction with optical absorbance measurements, the valence band maximum was calculated. These values demonstrate significant differences in the band positions of Cu_3SbSe_3 relative to other copper chalcogenide materials and may be used to rationalize failure of the heterojunctions we attempted. Using this knowledge, it is likely that a feasible n-type heterojunction material can be utilized to achieve the first photovoltaic device employing Cu_3SbSe_3 as an absorber layer. This development would have important implications for the search for alternative photovoltaic materials, as Cu_3SbSe_3 does not crystallize in a diamond-like lattice such as all the major thin-film photovoltaic materials, therefore broadening the criteria in the search for new solar absorbers.

APPENDIX A

SUPPORTING INFORMATION

7.1 Chapter 2: Ambient Surface Stability of Thin Film Nanocrystalline Cu_3SbSe_4 and Structure-Property Relationships

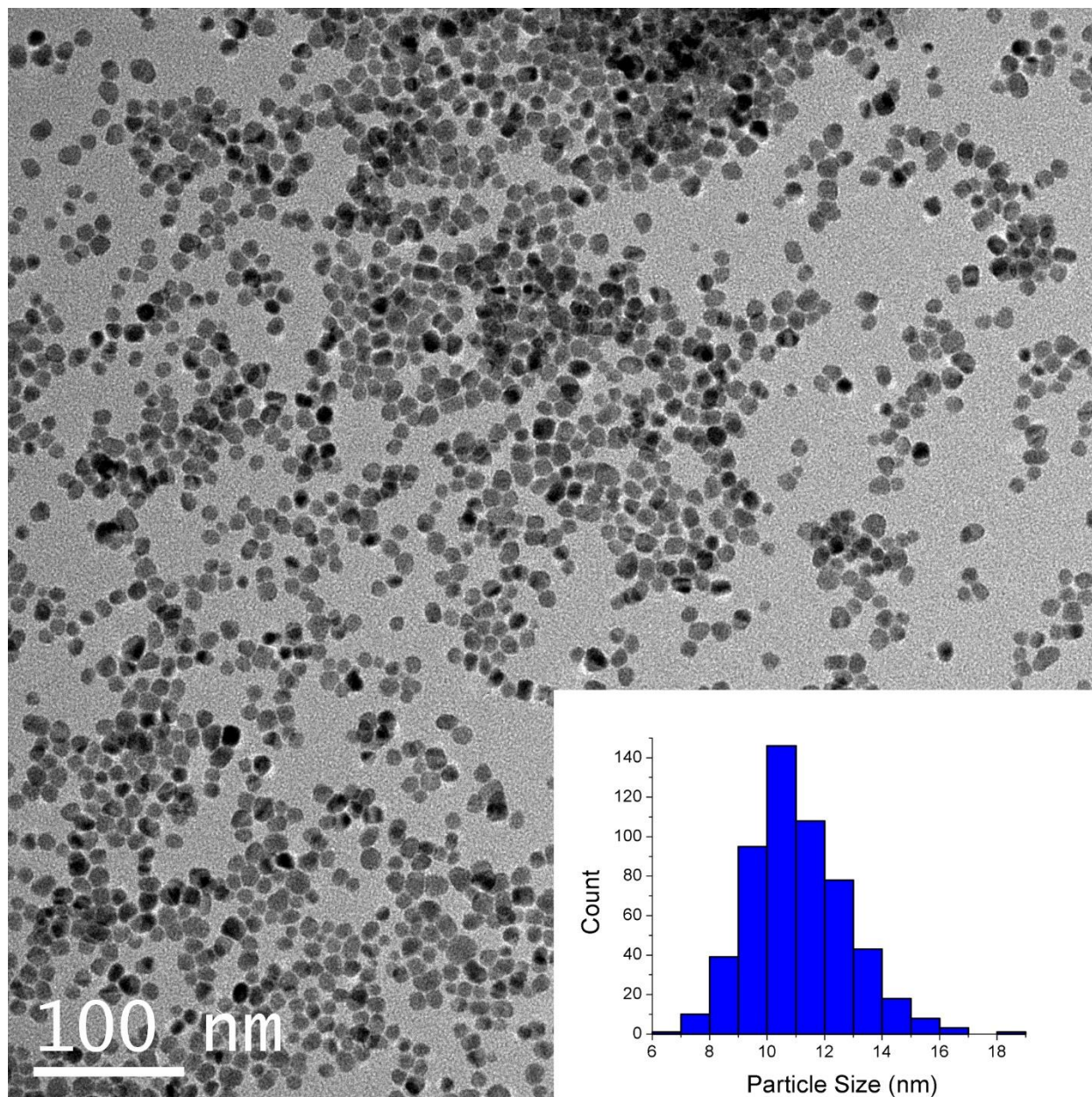


Figure S2.1. TEM particle size analysis. Particle sizes were measured using Digital Micrograph software. Particles were determined to be 11.1 ± 1.7 nm ($n = 550$ particles). Inset is the histogram demonstrating size distribution.

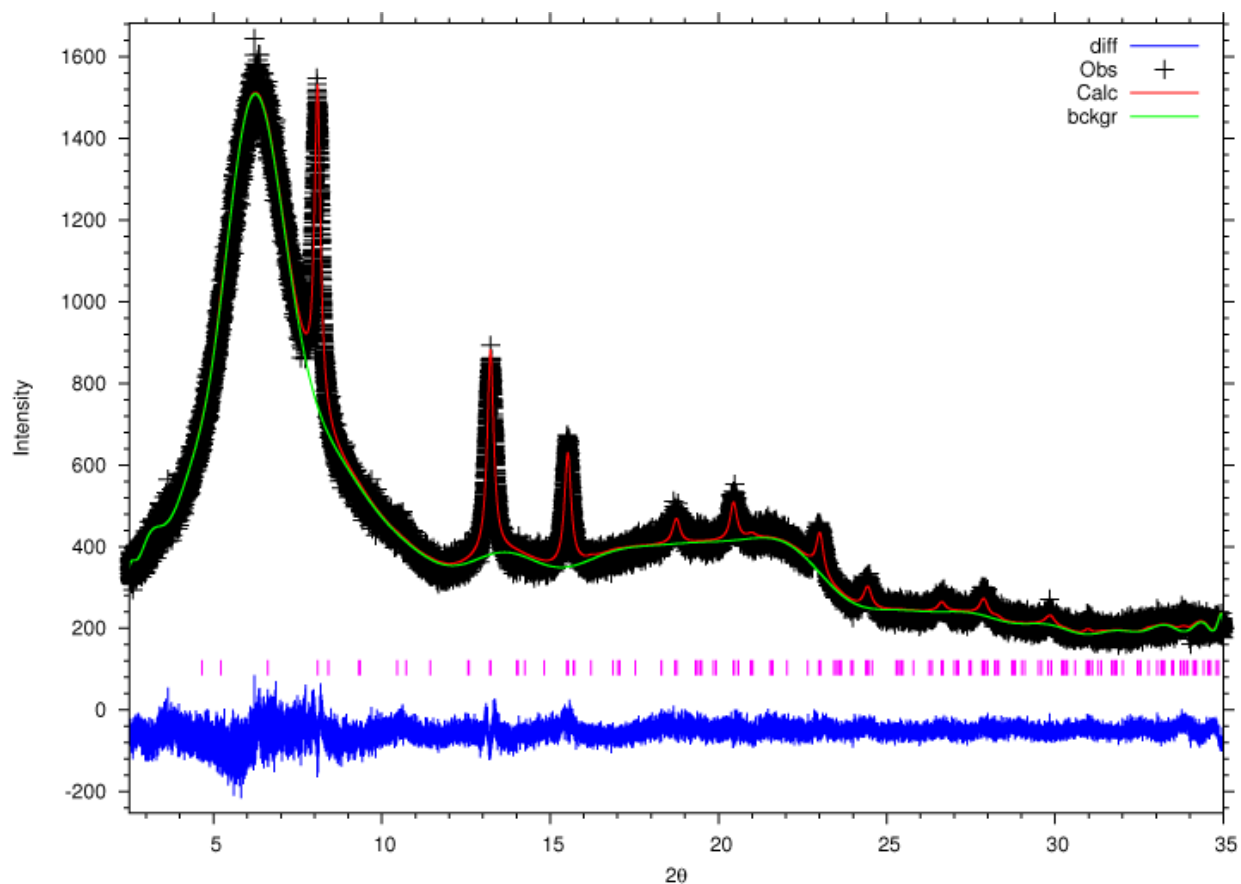


Figure S2.2. Rietveld calculations were performed on Cu_3SbSe_4 nanocrystal x-ray diffraction using synchrotron radiation ($\lambda=0.41 \text{ \AA}$). Diffraction of particles stored under inert conditions was compared with diffraction of particles exposed to ambient conditions. No significant changes were observed in crystallite size of the exposed or unexposed particles (box washed sample shown here, crystallite size=11.97 nm by Rietveld refinement), supporting HRTEM results which also show that the Cu_3SbSe_4 crystallite size does not change appreciably with oxidation.

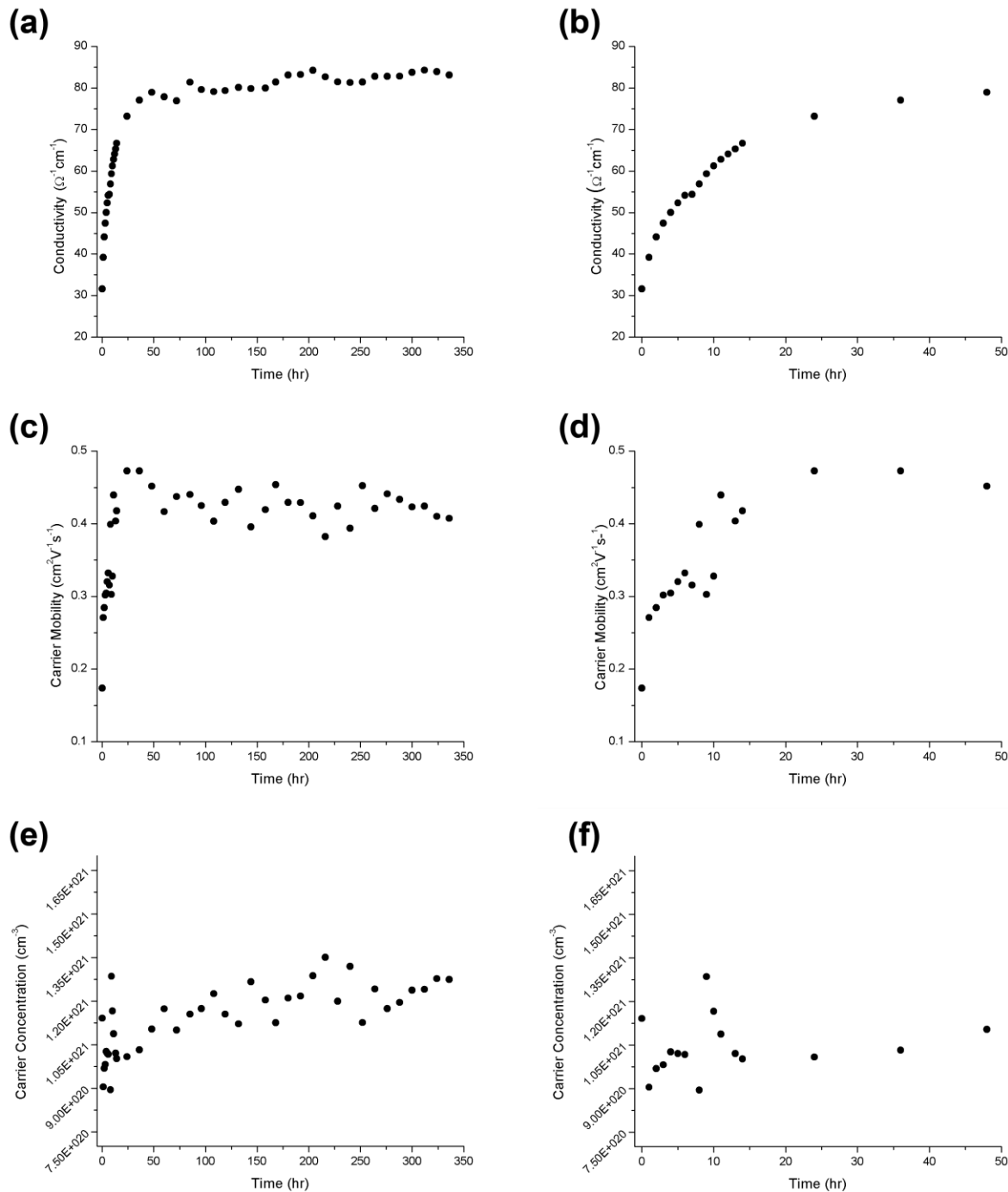


Figure S2.3. Electronic breakdown of champion Na_2S -exchanged Cu_3SbSe_4 film: (a), (c), and (e) exhibit electronic conductivity, hole mobility, and carrier concentration respectively over two weeks of measurements. To address the large initial increase in electronic conductivity, (b), (d), and (f) demonstrate the electronic conductivity, hole mobility, and carrier concentration over the first 50 hours, respectively. The initial increase in conductivity is attributed to an increase in mobility, possibly from the formation of an amorphous surface phase or oxide formation. The increase in overall conductivity at longer time lengths (>50 hours) is attributed to an increase in carrier concentration. This may be due to more complete oxidation of Cu^+ to Cu^{2+} as observed by XPS since this film was dipped on the benchtop, allowing all layers to be in contact with air throughout the dipping and measurement process

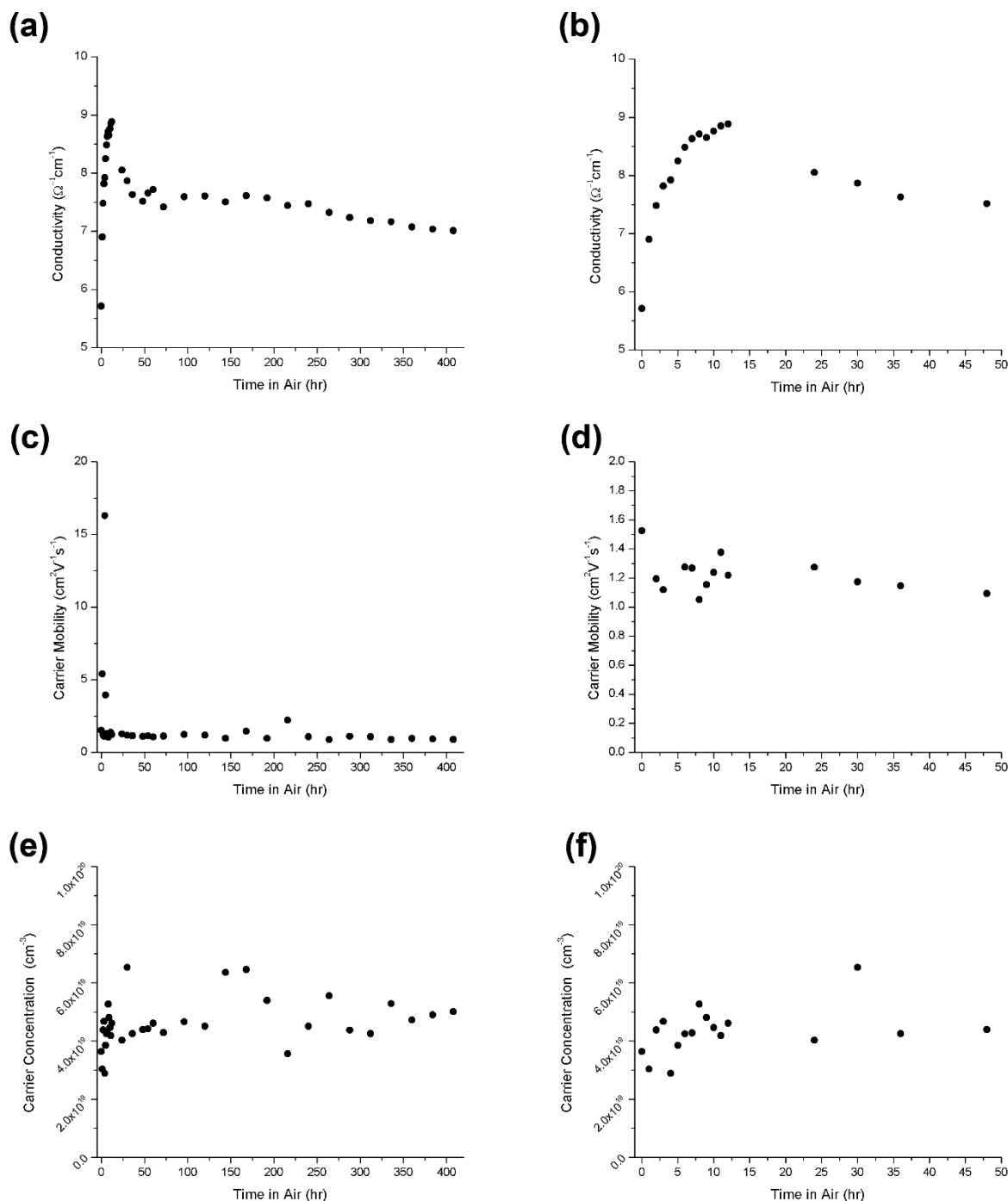


Figure S2.4. To establish a control, a film was dipped in an N₂ glovebox under inert conditions before removal for immediate application of gold contacts and measurement. Electronic conductivity (a), hall mobility (c), and carrier concentration (e) were measured for an extended period of time, with (b), (d), and (f) providing a closer analysis of the first 50 hours of these properties. It is observed that the film's conductivity is much lower than that dipped in air, though the mobility may be slightly higher. Therefore, the lower conductivity is attributed to a significantly lower carrier concentration. This may be due to the oxidation of Cu⁺ to Cu²⁺ acting as a hole dopant, so the inert-dipped film only exposes the surface to oxidation whereas the bench-dipped film exposes each layer. Also, the final film quality of the bench-dipped film was significantly more conformal, as a dip coder was employed whereas the films dipped under inert conditions were done by hand.

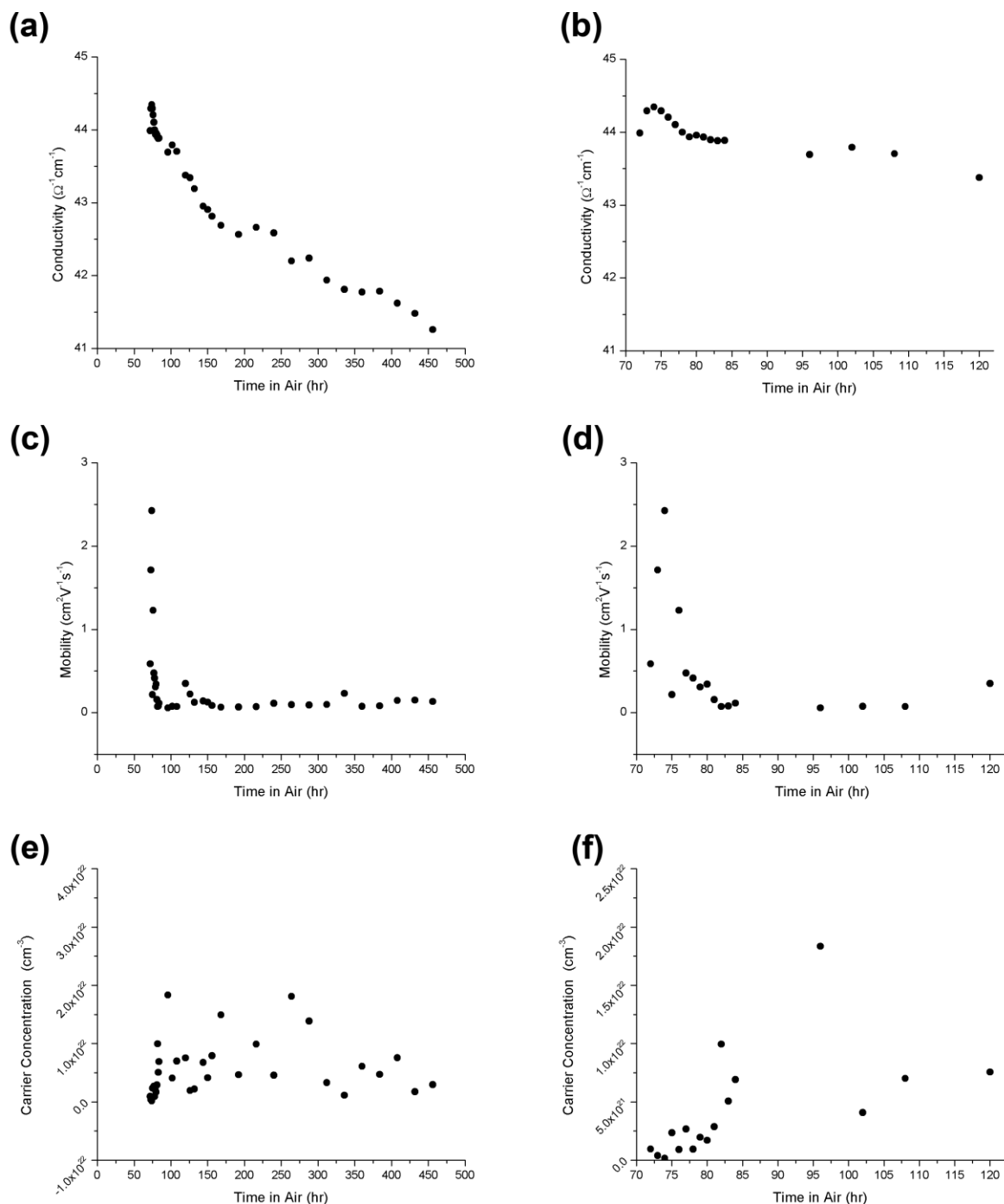


Figure S2.5. Hall measurements were taken of a film deposited under airfree washing and dipping conditions. The film was removed from the inert environment and stored under ambient conditions for three days at which point colloidal gold paste was used to apply contacts. Contacts were allowed ~5 minutes to set, and then Hall measurements began with this point being considered 72 hours on the “Time in Air” axis. These data show that the initial increase in conductivity is not due to the contacts setting, as there is only an initial increase in conductivity after ~3 hours, suggesting the contacts take a few hours to set, but the conductivity is limited to less than four hours (instead of two-to-three days, as is the length of time we observe an increase in electronic conductivity for films removed from an inert environment). In conjunction, the magnitude of the increase in the conductivity is significantly smaller for this film than the champion ($\sim 44 \rightarrow \sim 44.5 \Omega^{-1}\text{cm}^{-1}$ instead of $\sim 30 \rightarrow \sim 80 \Omega^{-1}\text{cm}^{-1}$). These suggest that the observed electronic conductivity increase is due to oxidation of the film.

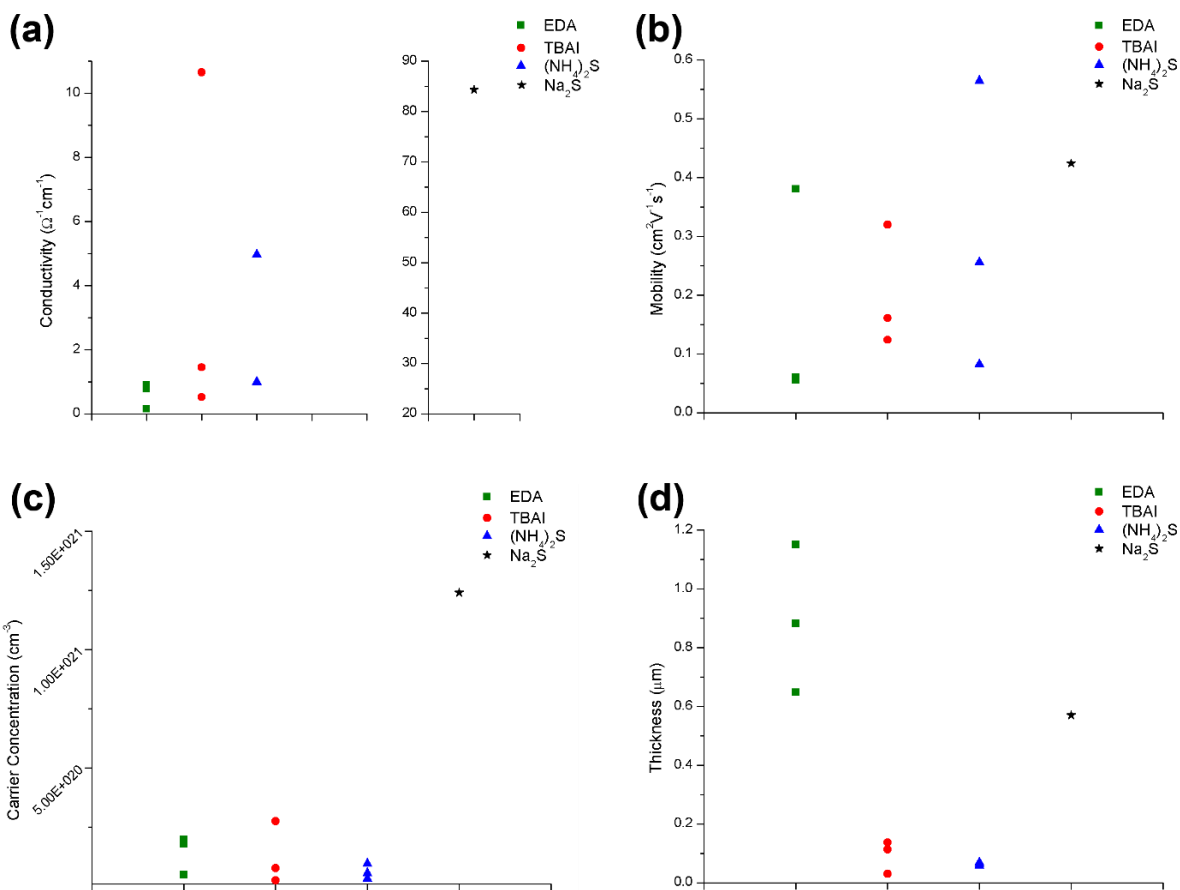


Figure S2.6. Several different ligand exchanges were performed and subsequently analyzed for their electronic properties: (a) electronic conductivity, (b) hole mobility, (c) carrier concentration, and (d) overall film thickness. Each exchange was performed in triplicate, and compared here to the data for the champion film (Na_2S -exchanged).

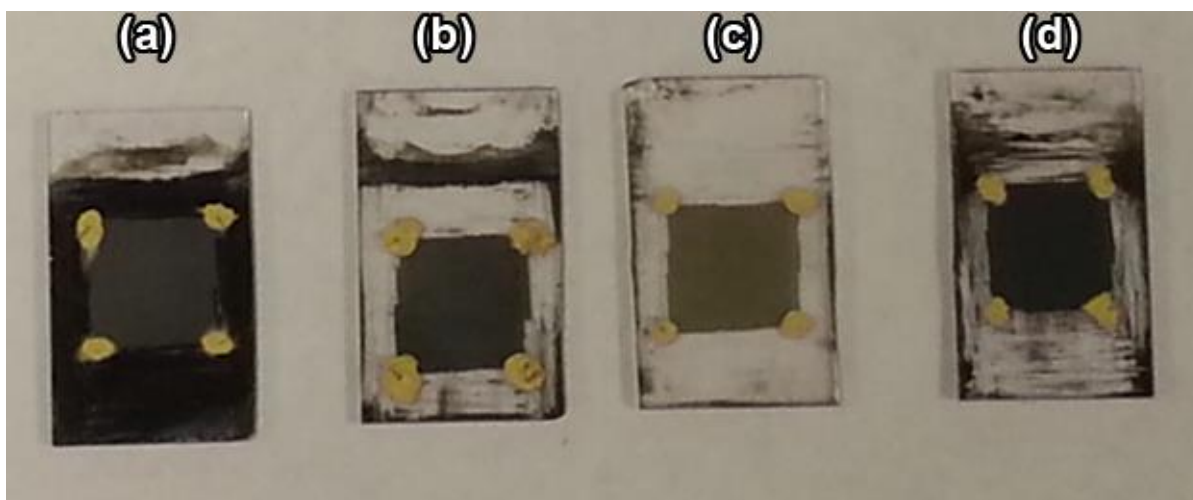


Figure S2.7. Photographs of ligand exchanged films were taken to compare film quality. From left to right: EDA (a), $(\text{NH}_4)_2\text{S}$ (b), and Na_2S (d). Following deposition, a 1 cm x 1 cm area was retained and the rest of the film was removed. Then gold Ohmic contacts were applied which can be seen on the corners of each film. It is clear that the $(\text{NH}_4)_2\text{S}$ films do not exchange well, resulting in a very thin optically translucent film. Contrary to this film, those dipped using ligand exchange with EDA, TBAI, and Na_2S exhibit good thickness and opacity demonstrating that they absorb light.

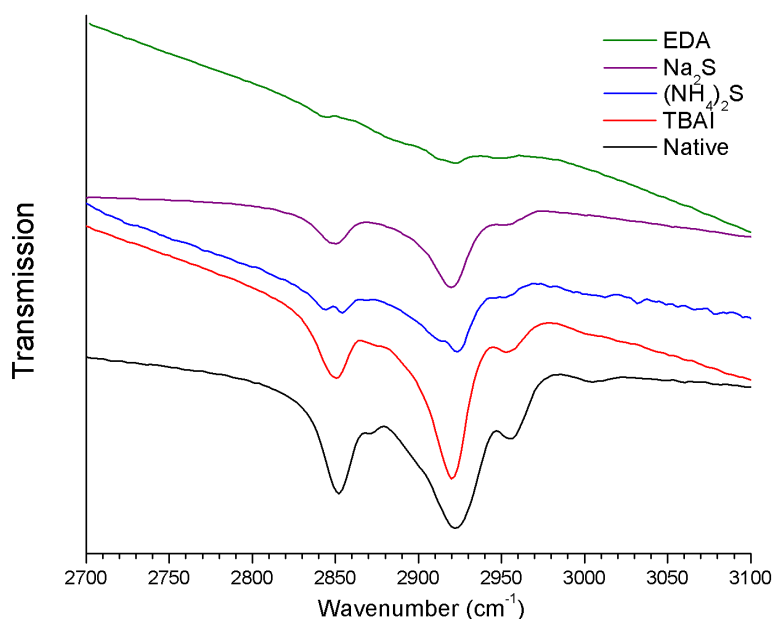


Figure S2.9. To roughly analyze the degree to which each ligand was able to supplant the native surface ligands, FTIR spectra were obtained of exchanged films, and of a film dropcast with unexchanged particles. The intensity of C-H stretching around 2850 and 2925 cm^{-1} decreased in all ligand exchanges, with respect to the observed intensity of the native ligand film in all cases indicative of a ligand exchange for a certain extent.

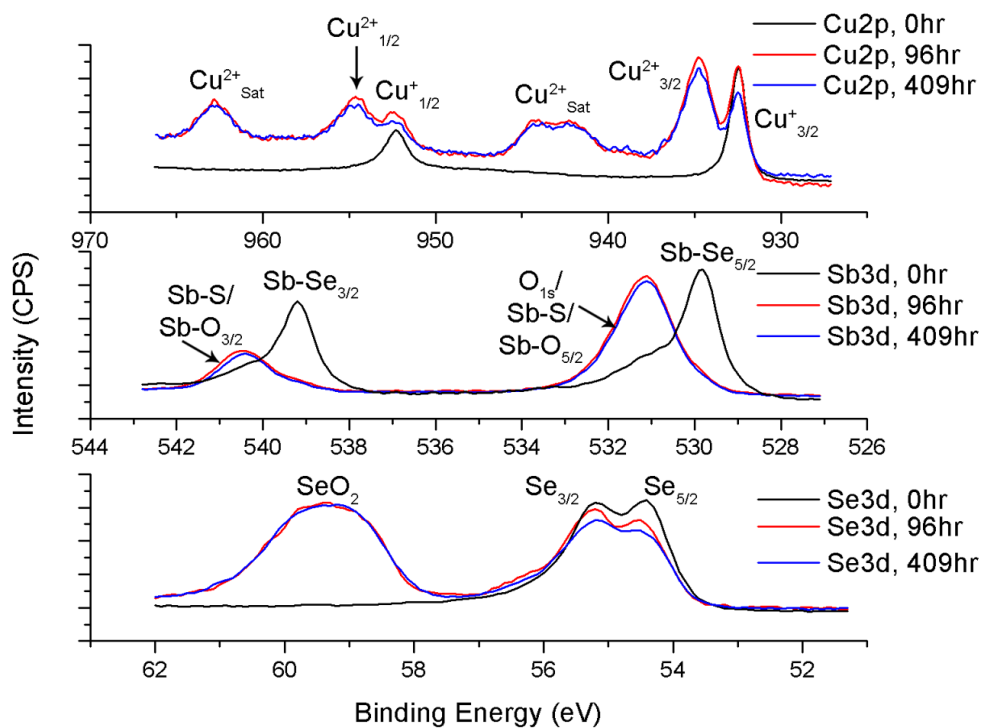


Figure S2.8. XPS comparisons of Cu_3SbSe_4 film kept under inert conditions (black), and then oxidized 96 hours (red) and 409 hours (blue). Top: Cu2p, middle: Sb3d, bottom: Se3d. Spectra are overlaid for visualization of growth of oxidized peaks.

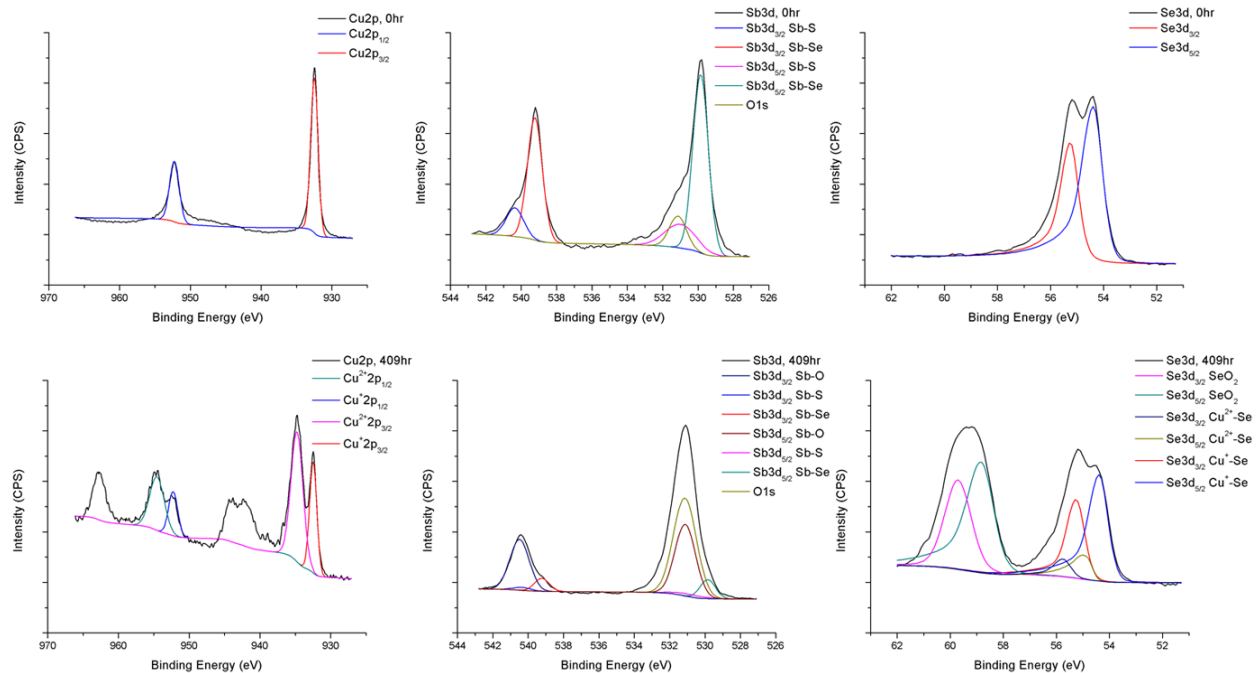


Figure S2.10. XPS fits of unexposed film (top row: Cu2p, Sb3d, Se3d, left to right) and film exposed 409 hours to ambient conditions (bottom row: Cu2P, Sb3d, Se3d, left to right).

Tables S1-S3. XPS Fitting Information

Cu2p, Sb3d, and O1s species were all fit with a Gaussian peak shape, and Se3d species were fit using an Asymmetric peak shape. All peaks utilized a Shirley background. Peak separation between Cu2p peaks was 19.80 eV, between Sb3d peaks was 9.37 eV, and between Se3d peaks was 0.87 eV.

Table S1: XPS Fitting Cu2p

Species	Time Aged (hr)	Environment	Position (eV)	Area	Area Normalized
Cu2p _{1/2}	0	Cu ⁺ , CuSe ₄ tetrahedra	952.26	7076	1
Cu2p _{3/2}	0	Cu ⁺ , CuSe ₄ tetrahedra	932.47	14152	2.00
Cu2p _{1/2}	96	Cu ²⁺ 2p _{1/2} Satellite	962.68	1369	1.46
Cu2p _{1/2}	96	Cu ²⁺ , CuSe ₄ tetrahedra	954.56	1766	1.88
Cu2p _{1/2}	96	Cu ⁺ , CuSe ₄ tetrahedra	952.27	939	1
Cu2p _{3/2}	96	Cu ²⁺ 2p _{3/2} Satellite	943.11	2123	2.26
Cu2p _{3/2}	96	Cu ²⁺ , CuSe ₄ tetrahedra	934.76	3531	3.76
Cu2p _{3/2}	96	Cu ⁺ , CuSe ₄ tetrahedra	932.47	1879	2.00
Cu2p _{1/2}	409	Cu ²⁺ 2p _{1/2} Satellite	962.72	1058	1.49
Cu2p _{1/2}	409	Cu ²⁺ , CuSe ₄ tetrahedra	954.56	1369	1.93
Cu2p _{1/2}	409	Cu ⁺ , CuSe ₄ tetrahedra	952.27	710	1
Cu2p _{3/2}	409	Cu ²⁺ 2p _{3/2} Satellite	943.11	1693	2.38
Cu2p _{3/2}	409	Cu ²⁺ , CuSe ₄ tetrahedra	934.76	2737	3.85
Cu2p _{3/2}	409	Cu ⁺ , CuSe ₄ tetrahedra	932.47	1419	2.00

Note: for “area normalized”, the peak area was normalized to the area of Cu⁺2p_{1/2} for each respective sample, as this should be the native crystal structure environment for Cu in Cu₃SbSe₄, and as such should be present in all samples. It can be seen that over time, the relative intensities of Cu²⁺:Cu⁺ are similar, suggesting that the oxidation process is complete after 96 hours, which correlates well with observed changes in electronic conductivity through Hall measurements. This relationship can be seen with the other oxidation environments as is shown in the area tables for Sb3d and Se3d peak fitting.

Table S2: XPS Fitting Sb3d

Species	Time Aged (hr)	Environment	Position (eV)	Area	Area Normalized
Sb3d _{3/2}	0	Sb-S	540.36	1387	0.27
Sb3d _{3/2}	0	Sb-Se	539.23	5171	1
Sb3d _{5/2}	0	Sb-S	530.99	2081	0.40
Sb3d _{5/2}	0	Sb-Se	529.85	7756	1.50
O1s	0	O	531.14	1498	0.29
Sb3d _{3/2}	96	Sb-O	540.49	6147	5.15
Sb3d _{3/2}	96	Sb-S	540.36	320	0.27
Sb3d _{3/2}	96	Sb-Se	539.22	1193	1
Sb3d _{5/2}	96	Sb-O	531.12	9221	7.73
Sb3d _{5/2}	96	Sb-S	530.99	480	0.40
Sb3d _{5/2}	96	Sb-Se	529.85	1789	1.50
O1s	96	O	531.14	12503	10.48
Sb3d _{3/2}	409	Sb-O	540.49	4833	5.10
Sb3d _{3/2}	409	Sb-S	540.35	254	0.27
Sb3d _{3/2}	409	Sb-Se	539.22	947	1
Sb3d _{5/2}	409	Sb-O	531.12	7249	7.65
Sb3d _{5/2}	409	Sb-S	530.98	381	0.40
Sb3d _{5/2}	409	Sb-Se	529.85	1421	1.50
O1s	409	O	531.14	11075	11.69

Sb spectra demonstrate the growth of a Sb-O environment after exposure to air for an extended period of time. A small amount of O1s is observed without any prolonged aging, and this is attributed to the exposure involved in transporting the sample from the inert atmosphere to the instrument for measurement.

Table S3: XPS Fitting Se3d

Species	Time Aged (hr)	Environment	Position (eV)	Area	Area Normalized
Se3d _{3/2}	0	Cu ⁺ Sb-Se	55.26	2629	1
Se3d _{5/2}	0	Cu ⁺ Sb-Se	54.39	3944	1.50
Se3d _{3/2}	96	SeO ₂	59.71	882	1.25
Se3d _{5/2}	96	SeO ₂	58.84	1324	1.88
Se3d _{3/2}	96	Cu ²⁺ Sb-Se	55.75	139	0.20
Se3d _{3/2}	96	Cu ⁺ Sb-Se	55.26	705	1
Se3d _{5/2}	96	Cu ²⁺ Sb-Se	54.88	209	0.30
Se3d _{5/2}	96	Cu ⁺ Sb-Se	54.39	1057	1.50
Se3d _{3/2}	409	SeO ₂	59.71	727	1.44
Se3d _{5/2}	409	SeO ₂	58.84	1091	2.16
Se3d _{3/2}	409	Cu ²⁺ Sb-Se	55.75	113	0.22
Se3d _{3/2}	409	Cu ⁺ Sb-Se	55.26	506	1
Se3d _{5/2}	409	Cu ²⁺ Sb-Se	54.88	169	0.33
Se3d _{5/2}	409	Cu ⁺ Sb-Se	54.39	759	1.5

Similarly to the results seen in the Sb spectra, Se spectra exhibit a strong growth of peaks related to SeO₂. Of further interest is the appearance of a higher binding environment peak, which we attribute to coordination to Cu²⁺ species in place of the native Cu⁺ environment.

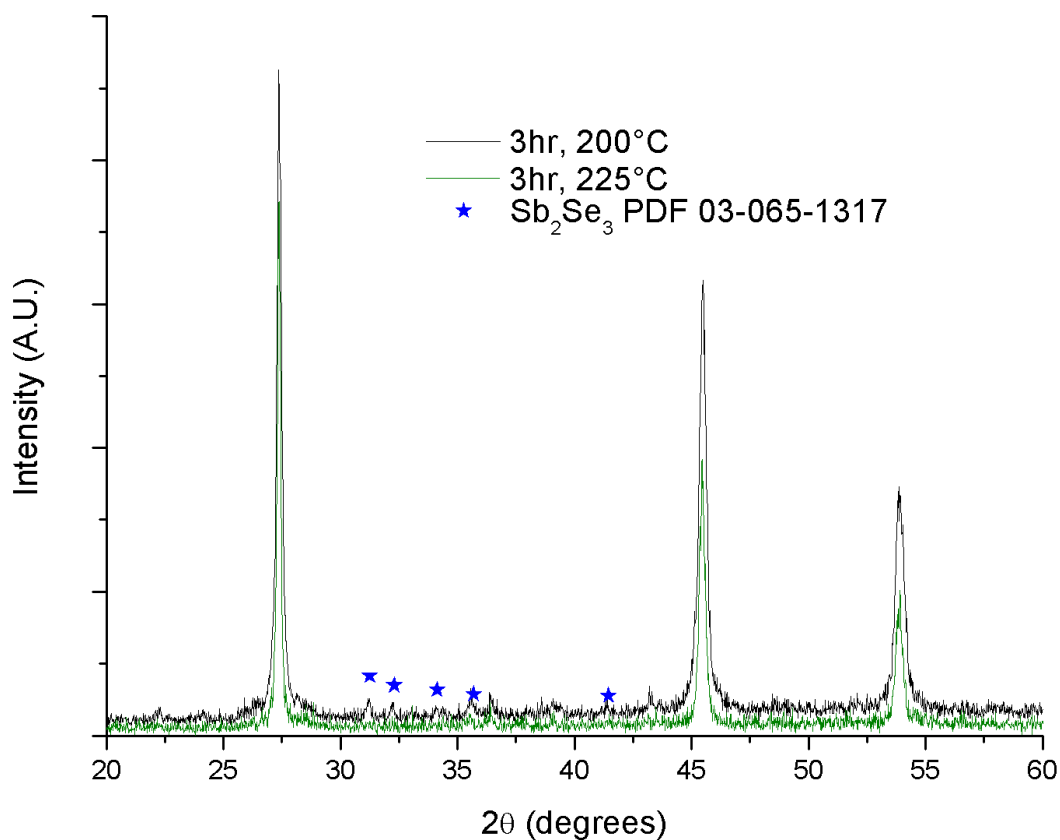


Figure S2.11. Another synthetic route we explored for the synthesis of Cu_3SbSe_4 nanocrystals was the injection of the CuCl_2/OLA complex into $\text{SbCl}_3/\text{Se}/\text{OLA}$. These reactions require longer growth times (on the order of hours as opposed to minutes), and were determined to proceed by Cu diffusion into Sb_2Se_3 . The Sb_2Se_3 phase can be isolated if the injection is never performed, and the reaction proceeds faster at higher temperatures, as expected for a diffusion process (phase purity was obtained in 3 hours at 225 °C while at 200 °C the reaction requires 4 hours to proceed to a single phase sample).

7.2 Chapter 3: Hot-Injection Route for Synthesis of Cu_3SbSe_3 Nanodiscs and Investigation of Structural Anisotropy

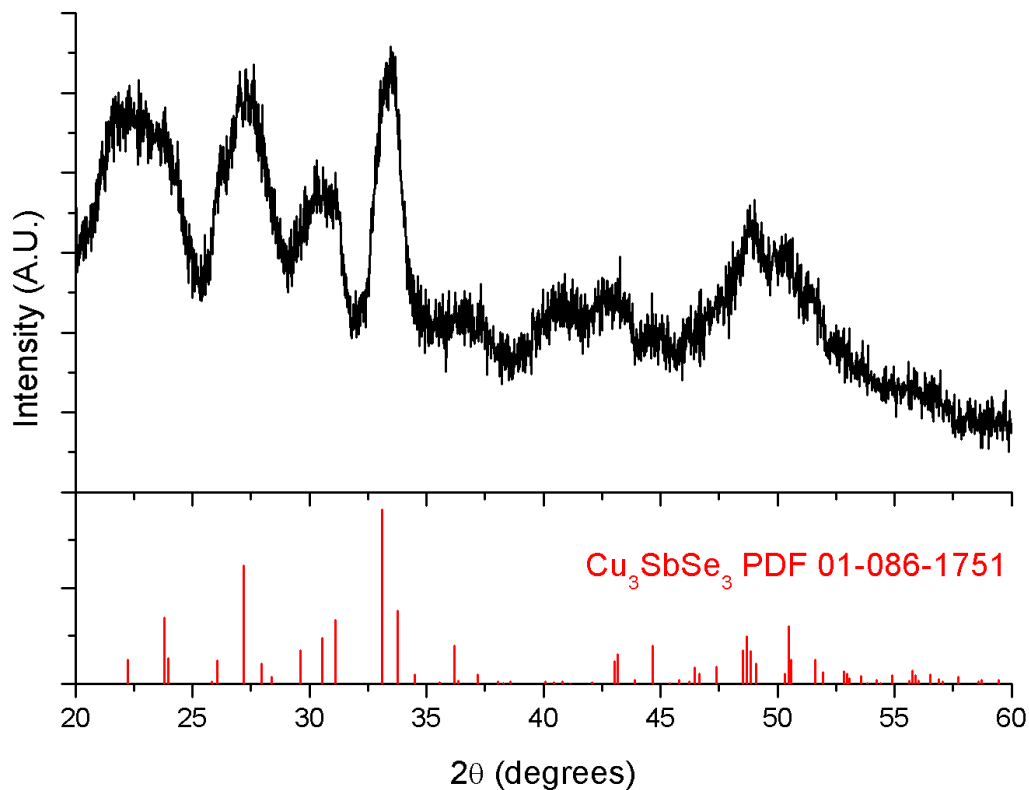


Figure S3.12. X-ray diffraction pattern of Cu_3SbSe_3 nanodiscs. Significant peak broadening is attributed to the small crystallite size of the nanodiscs, though all observed peaks can be indexed to Cu_3SbSe_3 (with the exception of the hump from 38–44 $^\circ 2\theta$, as this occurs due to the sample holder). Some preferential orientation can be observed at $\sim 22^\circ 2\theta$, attributed to the flat orientation of the discs.

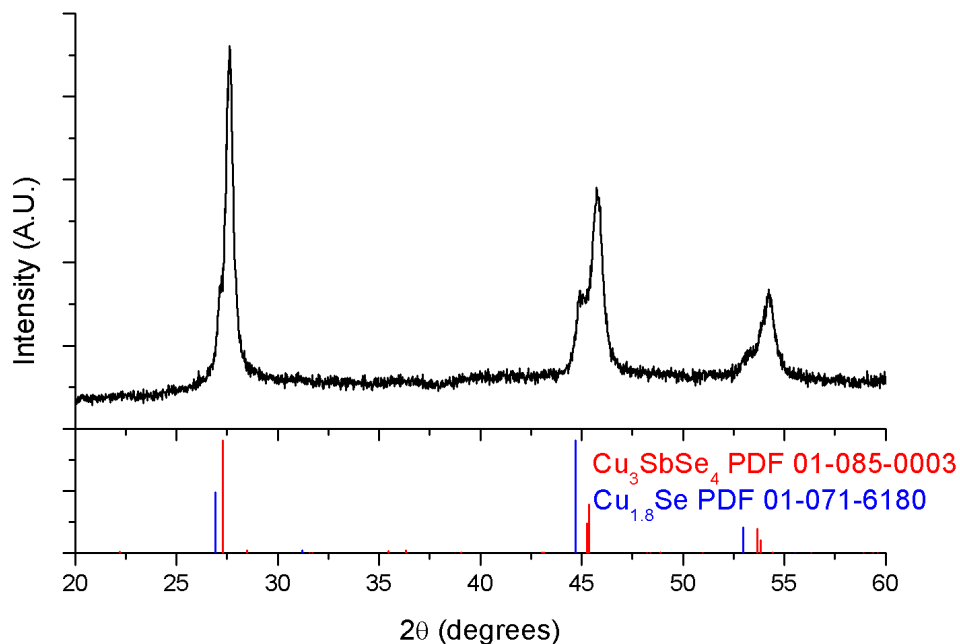


Figure S3.13. XRD pattern of crystals formed by injection of Se/oleylamine/ethanethiol. The use of ethanethiol in place of dodecanethiol results in Cu_3SbSe_4 and $\text{Cu}_{1.8}\text{Se}$ instead of Cu_3SbSe_3 .

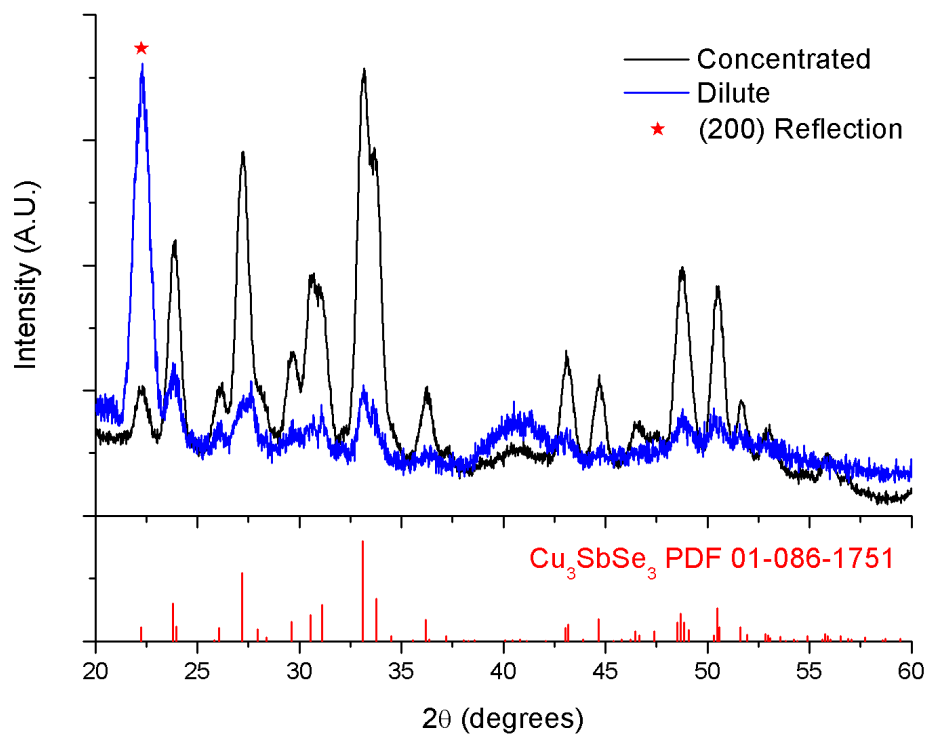


Figure S3.14. XRD pattern emphasizing the (200) peak. Dilute suspensions relax to allow the discs to lie flat against the substrate leading to an increased intensity of the (200) peak due to preferential orientation, denoted by the red star. Note: broad peak from 38-44° 2θ is due to the sample holder. Note: synthesis employed is described in chapter 4.

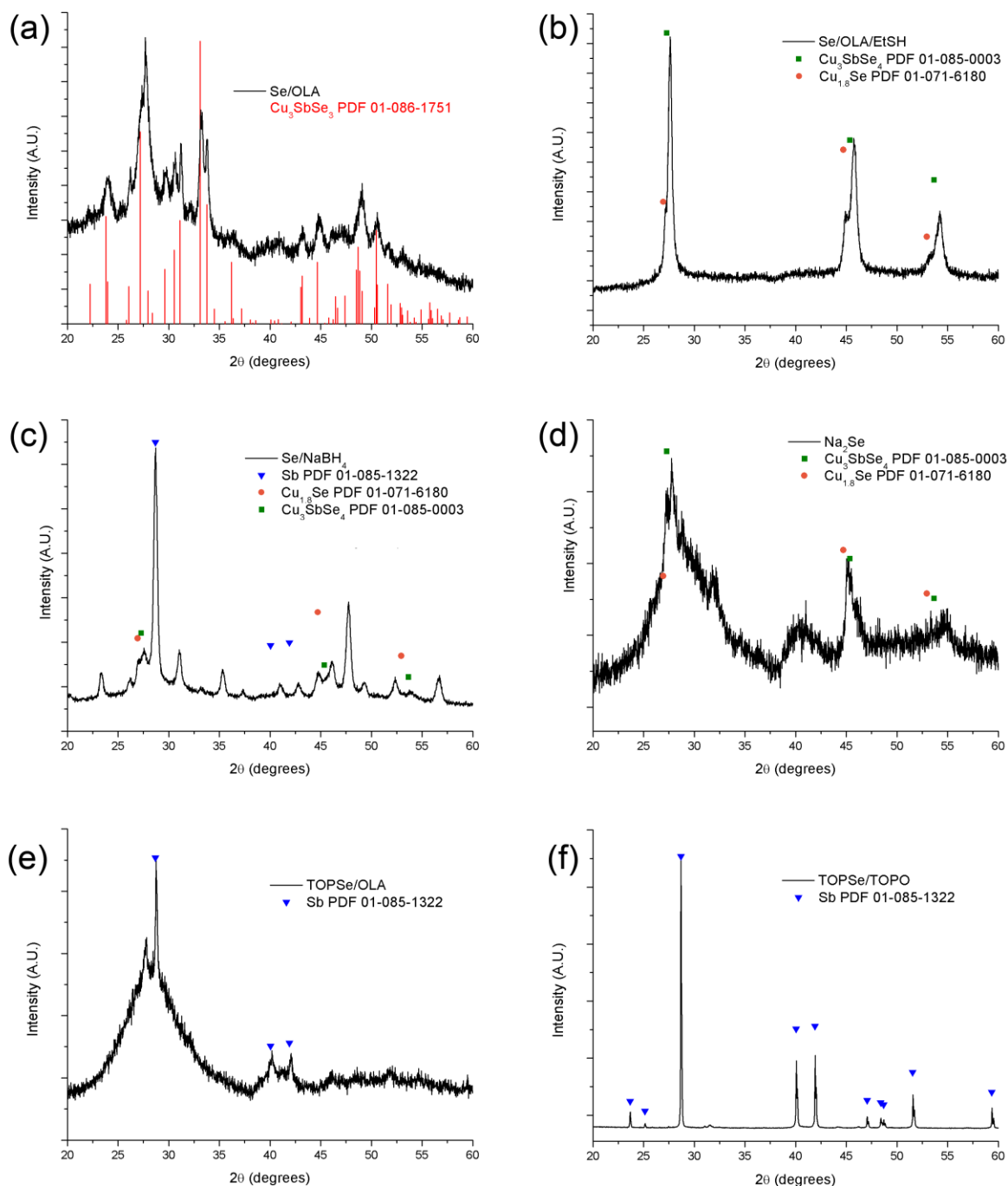


Figure S3.15. XRD patterns of thiol-free selenium injections. a) Molten selenium in oleylamine yields Cu_3SbSe_3 with a broad peak at $28^\circ 2\theta$, b) selenium dissolved in a mixture of oleylamine and ethanethiol (with the thiol removed via heat and vacuum) yields a mixture of Cu_3SbSe_4 and $\text{Cu}_{1.8}\text{Se}$, c) forced reduction of selenium using NaBH_4 yields a mixture of metallic Sb along with the possibility of Cu_3SbSe_4 and/or $\text{Cu}_{1.8}\text{Se}$ along with other unidentified crystalline impurities, d) Na_2Se yields Cu_3SbSe_4 and/or $\text{Cu}_{1.8}\text{Se}$ despite the reagent's insolubility in oleylamine, e) TOPSe injected into an OLA solution of metals produces metallic antimony and an amorphous solid, while f) TOPSe injected into a solution of metal precursors dissolved in TOPO produces phase-pure metallic antimony.

7.3 Chapter 4: Understanding Growth and Stacking of Cu₃SbSe₃ Nanodiscs

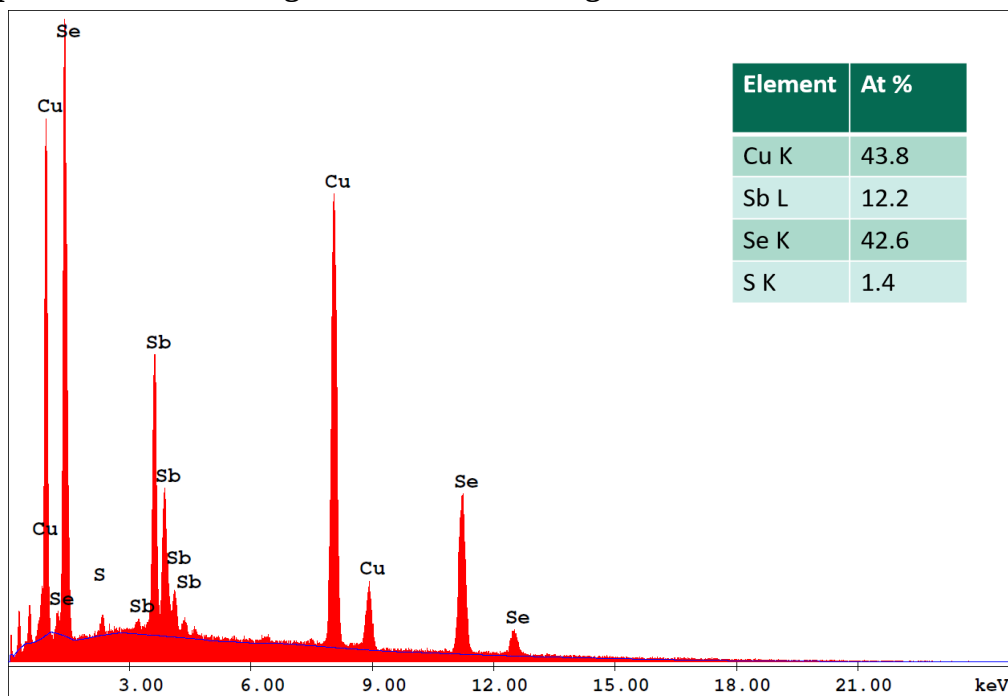


Figure S4.16 Energy dispersive X-ray spectrum (EDS) of Cu₃SbSe₃ nanodiscs. Peaks at lower energy than Cu index to N and O, likely present from oleylamine and air.

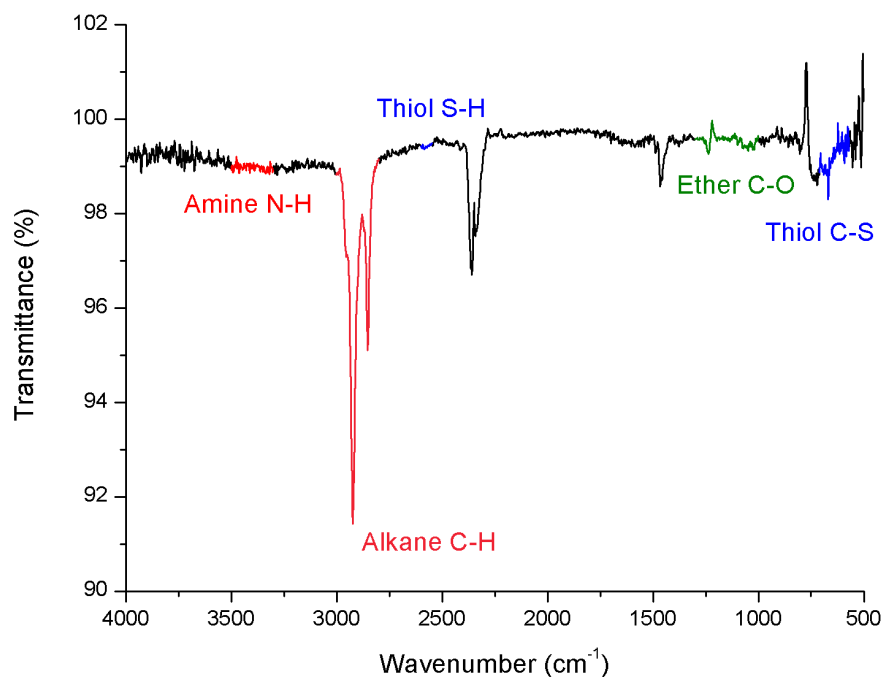


Figure S4.17 FTIR spectrum of nanodiscs synthesized via double-injection. Strong C-H bonds are observed indicating the presence of organic ligands. However, unambiguous characterization of the presence of diphenyl ether, oleylamine, and/or dodecanethiol is convoluted as moieties indicative of these ligands are not present. This is expected as these ligands coordinate to the nanocrystalline surface through their unique functional groups.

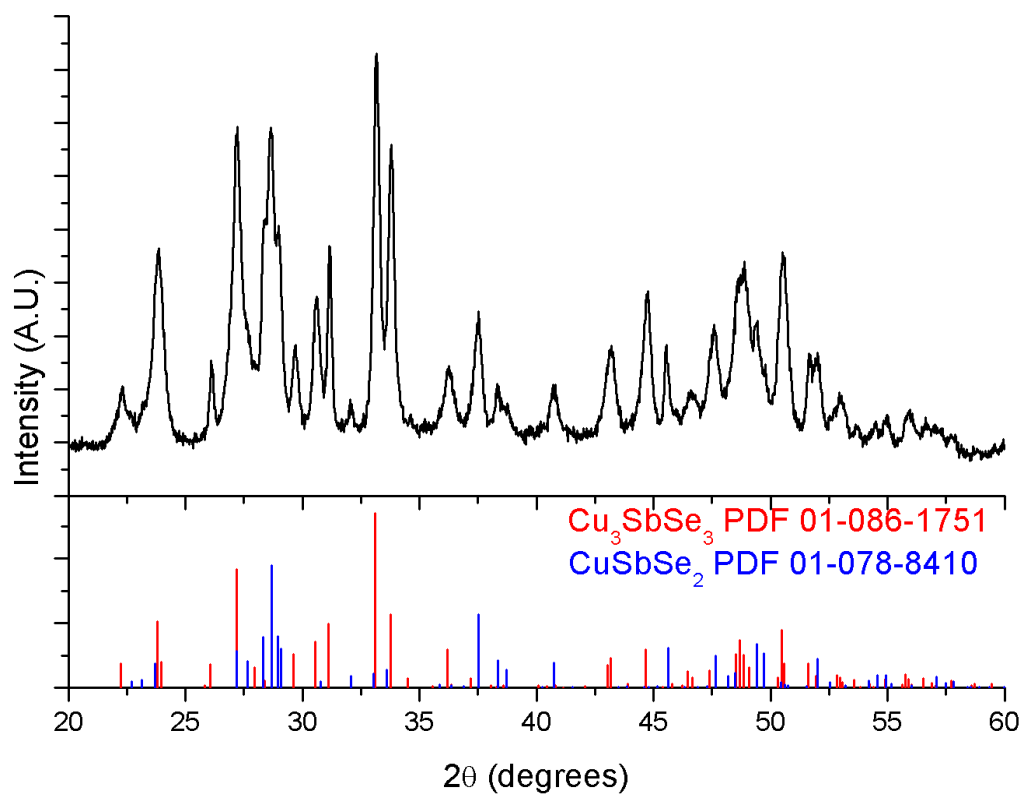


Figure S4.18 XRD Pattern of double injection Cu_3SbSe_3 synthesized in large excess diphenyl ether. Additional peaks were indexed to CuSbSe_2 , though it is important to note that the primary method of ensuring phase purity is through suspension and precipitation cycles, though the products of this reaction do not suspend.

7.4 Chapter 5: Electrochemical Methods for the Electrical Characterization of Cu_3SbSe_3 Nanodiscs

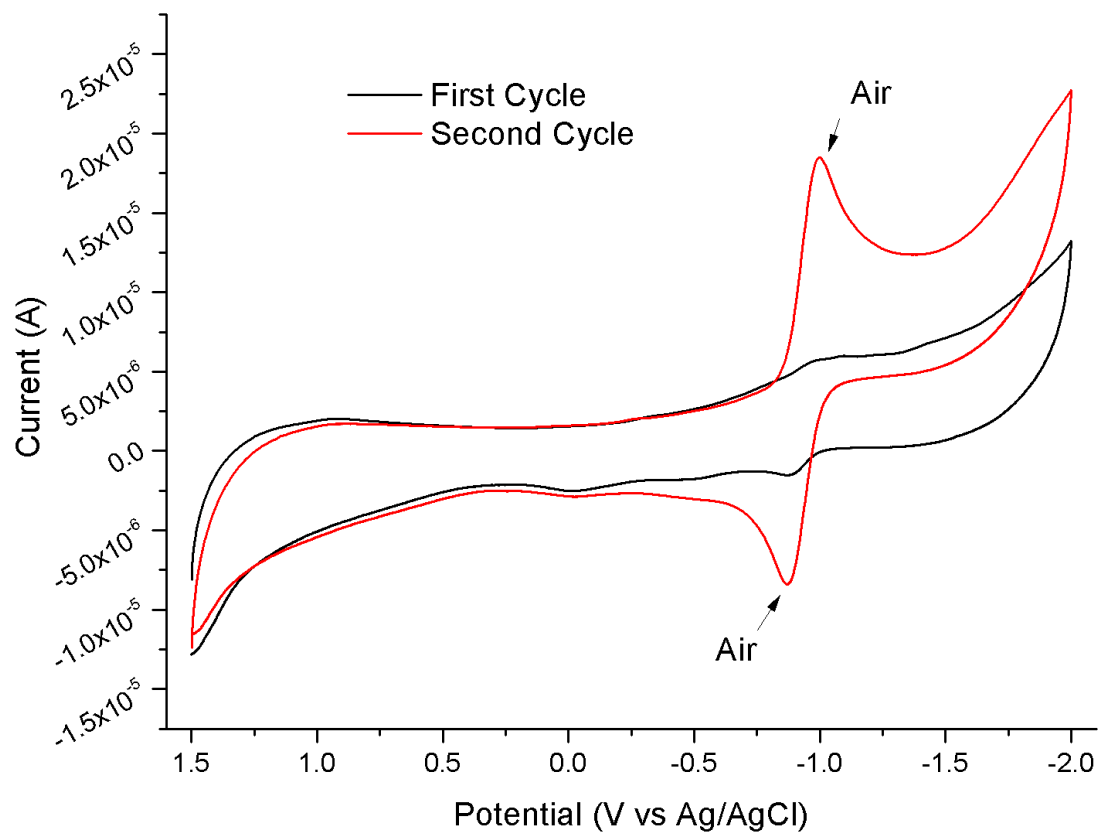


Figure S5.19. Cyclic voltammograms of 0.1 M TBAPF₆ in MeCN on a cleaned glassy carbon working electrode. Prior to measurement, the solution was degassed by sparging with N₂. A peak grows in at -0.92 V vs Ag/AgCl with time and is attributed to the exposure to air.

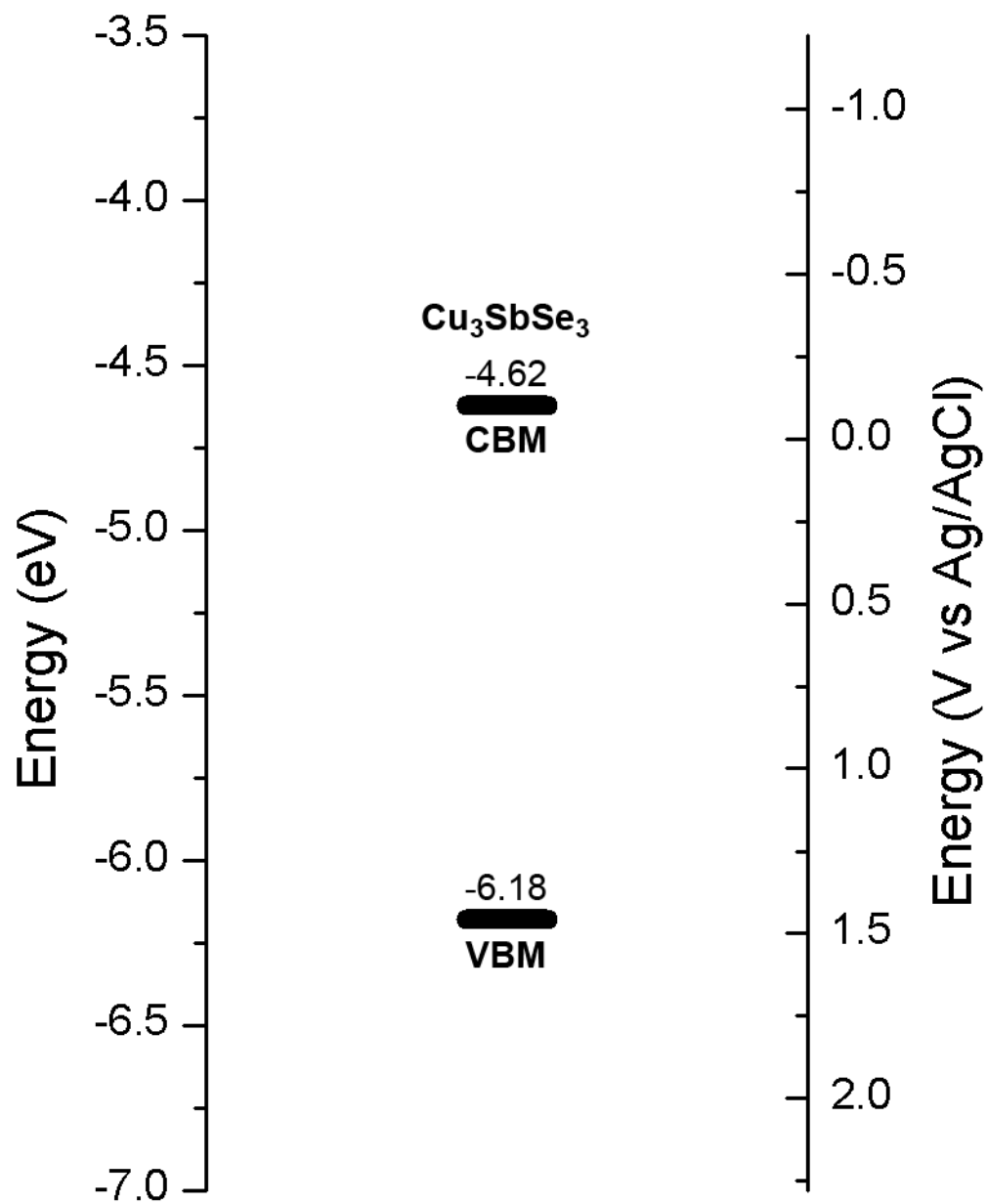


Figure S5.20. Conversion from Ag/AgCl reference to vacuum level. Band positions for Cu_3SbSe_3 are reported for the CBM found by CV (Figure 5.1) and the VBM by subtracting the optical band gap obtained from UV-Vis (Figure 4.3).