AN ABSTRACT OF THE DISSERTATION OF

<u>Vorranutch Jieratum</u> for the degree of <u>Doctor of Philosophy</u> in <u>Chemistry</u> presented on <u>June 12, 2012.</u>

Title: Iron and Copper Chalcogenides: Photovoltaic Absorber Candidates and YZrF₇: A New Upconversion Host

Abstract approved: ____

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The materials $Fe_2(Si,Ge)(S,Se)_4$, $Cu_3PS_{4-x}Se_x$ ($0 \le x \le 4$), and $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$) have been synthesized and studied as new earth-abundant absorbers for single and multijunction photovoltaic cells as well as solar fuel generation. The synthesis, single-crystal growth, and optical and electrical properties of these materials are described and discussed in Chapter 2, 3, and 4. Inspired by the photovoltaic absorber Cu_2ZnSnS_4 , the new compound $CuZnPS_4$ has been discovered; its structure and properties are discussed in Chapter 5, including a comparative analysis to Cu_3PS_4 . The compound $YZrF_7$ (Chapter 6) has been synthesized and evaluated for the first time as a new optical host for green up-conversion.

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Iron and Copper Chalcogenides: Photovoltaic Absorber Candidates and

YZrF7: A New Upconversion Host

by

Vorranutch Jieratum

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Vorranutch Jieratum, Author

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Iron and Copper Chalcogenides: Photovoltaic Absorber

Candidates and YZrF₇: A New Upconversion Host

Chapter 1

Introduction

1.1 Need of Renewable energy

"The terawatt challenge" refers to the world's rapidly increasing demand for energy beyond 13 TW/year and the need for clean energy sources. [1] As global warming issues associated with CO₂ emissions and fossil fuel consumption accelerate, carbon-free, renewable, and sustainable energy sources become the best approach to addressing climate change. Sources of energy beyond fossil fuels, such as nuclear, hydroelectricity, wind, and solar power, are important for production of electricity to address the needs of a growing population without destroying the environment. Nuclear power, the only proven large-scale carbon-free technology seems attractive, but, safety, radioactive-waste disposal, and limited natural abundance of uranium and plutonium raise concerns about scaling and sustainability. Hydroelectricity and wind are important contributors to the overall energy landscape, and wind, in particular, has seen dramatic growth over the past decade. About 120,000 TW of sunlight strikes the earth each hour [1] - more energy than the entire population of the world consumes in a year. Hence, energy from the sun is essentially unlimited, if only it could be converted directly to electricity or fuels at a competitive cost.

It has been proposed that photovoltaic (PV) technologies could meet global energy consumption by covering ~0.4% of the earth's land area with solar cells having an efficiency of 10%. [1,2] The cost, however, to achieve this goal is simply too high relative to competing technologies, i.e., >20 cents/kW h in a typical polycrystalline-Si PV cell with over 20 year lifetime, 4-10 cents/kW h for wind energy and 5-7 cents/kW h for natural gas. [3] Materials play an important role in determining the cost of a solar module. Hence, the development of low cost materials that enable improvements efficiencies of PV devices is crucial to making solar energy a competitive, large-scale energy sources.

1.2 Photovoltaic cells, efficiency and Photovoltaic absorbers

Photovoltaic (PV) devices generate direct current (DC) electrical power from semiconductors when they are illuminated by photons. [2] Sometimes we use "solar cell" as a common name for a PV cell, since our source of photons is the sun. The semiconductor absorbing the light is a solar absorber or PV absorber. A PV cell consists of a *p*-type semiconductors layer, where the majority carriers are holes, and *n*-type semiconductors layer, where the majority carriers are holes, and *n*-type semiconductors layer having a very low intrinsic carrier concentration. These semiconductors are integrated to form p-n or p-i-n diodes, which enable current following photogeneration of electron-hole pairs (e^{-}/h^{+}).



Figure 1.1 Energy band diagram of a typical p-i-n thin-film PV cell.

Fig. 1.1 represents energy band diagram of a typical p-i-n thin-film PV cell. The nlayer is an n-type transparent conductor, the i-layer is the solar absorber (usually p-type material), and the p-layer is a p-type semiconductor (or back contact). When such a cell is exposed to light (hv), electrons from the valence band (VB) are excited to the conduction band (CB), resulting in the generation of electron-hole pairs and subsequent separation induced by the electric-field gradient across the i-layer. This gradient accelerates electrons toward the n-layer and, holes toward the p-layer, enabling production of a current through an external load.

In general, the important figure of merit for a solar cell is its power conversion efficiency (η), which is defined [4] as:

$$\eta = P_{max}/P_{in} = (FF V_{oc} I_{sc})/(E_{tot} A)$$
(Eq. 1.1)

where, $P_{max} = peak PV power (I_{max} V_{max})$

- P_{in} = incident power, determined by the properties of the light spectrum incident upon the PV cell.
- $FF = fill factor = I_{max} V_{max} / I_{sc} V_{oc}$, a ratio of the area of the two rectangles in the I-V curve (Fig. 1.2) indicating the ideality of the device.
- V_{oc} = Open-circuit voltage, voltage I = 0 (Fig. 1.2).
- I_{sc} (or J_{sc}) = Short-circuit current, current V = 0 (Fig. 1.2).
- Etot = total energy of incident light
- A = cell (device) area



Figure 1.2 Current-voltage (I-V) curve.

 I_{sc} is related to the number of electron-hole pairs generated from light absorption by the PV absorber. V_{oc} is directly related to the optical band gap of the material, i.e., the larger the gap, the higher V_{oc} . Because P = IV, it is desirable to achieve a maximum in the IV product. Considering the shape of the solar spectrum, absorber band gaps from 1-1.6 eV are predicted by Shockley-Queisser to maximize the cell efficiency of a single p-n junction. [4, 5] For an AM1.5 global spectrum, the maximum theoretical efficiency associated with a band gap near 1.1 eV is 48%. [4] Theoretical limited efficiencies of multiple junctions are 50%, 56%, and 72% with 2, 3 and 36 band gaps, respectively. [6]

A p-type semiconductor is generally the preferred PV absorber, because the minority carriers contributing to the short-circuit current density are electrons, which typically have larger mobilities than holes. In this case, recombination of electron-holes pairs can be reduced, leading to higher current flow. Carrier lifetime and extraction efficiencies can increase in absorber layers containing low defect concentrations. The defect numbers can be correlated to carrier concentrations, where, as a general rule, carrier concentrations < 10^{18} cm⁻³ are desirable to realize efficient cells.

The absorption coefficient (α) describes how strongly a material absorbs light. High absorption ($\alpha > 10^5$ cm⁻¹) is desirable for thin-film solar cells, as it enables the use of very thin absorber layers. In such layers, carrier separation is aided by enhanced drift, providing a mechanism to realize very high efficiencies.

Nowadays, single-junction PV cells are based on crystalline Si, CdTe and Culn₁. _xGa_xSe₂ (CIGS); [2] records for these cells are 25% (2010) [7], 16.7% (2010) [7] and 20.3% (2011) [8], respectively. An efficiency of 41.6% in a multijunction cell of GalnP/ GalnAs/Ge has been reported by Spectrolab (USA). [7] Si technologies dominate the world's installed base of solar cells. While elemental Si is relatively inexpensive and certainly earth abundant, the high production costs of monocrystalline and polycrystalline wafer-based cells constrains widespread use. [9, 10] Much research has been focused on next generation thin film PV cells which use less material and require less tie and energy to fabricate. If coupled with high-efficiency performance, thin-film cells offer an opportunity to reduce costs and accelerate the widespread adoption of solar energy.

Current, commercial thin-film PV cells are based on CdTe and CIGS absorbers. Examples of single-junction CdTe and CIGS thin film PV cell diagrams [11, 12] are illustrated in Fig. 1.3. With laboratory efficiencies in the range of 10-20%, the technologies are promising, but considering the toxicity of cadmium and the high costs of rare indium and tellurium, their deployment at scales necessary to meet world-wide demands for clean energy is questionable.



Figure 1.3 Diagrams of thin film PV cell (a) Cu(In, Ga)Se₂ (CIGS) (b) CdTe. TCO stands for transparent conductive oxide.

Other promising solar cell configurations are multijunction PV cells [13] which provide approaches for capturing power and efficiency beyond the single junction approach. In this approach, semiconductior band gaps are matched to different spectral regions, with each semiconductor junction converting a select region of the spectrum to electricity (Fig. 1.4). Currently, the most successful material system for multijunction solar cells are based on III-V semiconductors, [13] although tandem cells are also known in thinfilm configuration containing amorphous Si and Ge and polycrystalline Si.



Photon energy (eV)

Figure 1.4 Diagram of three junction solar cells modified from [13, 14].

1.3 Properties related to electronic and crystal structure

The primary physical properties considered in identifying or designing a semiconductor absorber are optical band gap (direct gap preferred), absorption coefficient, *p*-type majority carriers, mobility, and carrier concentration. Since the most successful thin-film absorber up to now is Cu(In, Ga)Se₂ and Cu is readily available, Cu-based chalcogenide represent a prototypical platform for expanding and directing research on both known and unknown compounds as new solar absorbers.

The absorption coefficient at a given photon energy for a semiconductor is proportional to the probability for transition from an initial state to a final state and to the densities of initial and final electronic states as represented by the joint density of states. [15] The transitions between states near the valence band maximum (VBM) and the conduction band minimum (CBM) play a dominant role in determining absorption efficiency. Direct, allowed transitions (from selection rules) $d \rightarrow p, p \rightarrow d, p \rightarrow s$, and $s \rightarrow p$ are preferred. The density of states (DOS) is high in transition-metal chalcogenides, e.g. $Cu^+ (d^{10}), Fe^{2+} (d^6), Cd^{2+} (d^{10}),$ where the d states, contribute near the VBM, and the empty s states near the CBM. Through covalent bonding, anions, such as S^{2-} , Se^{2-} , and Te^{2-} , contribute significant p states density to both the VMB and the CBM. In ternary systems, such as CulnS₂, CulnSe₂, CuGaSe₂, In³⁺ and Ga³⁺ provide s and p states. Other p-block elements can contribute in similar a fashion. Crystal structure, composition, and atomic solid-state energies [16], and element size affect band dispersion, and the DOS of p states near the VBM and the CBM.

Band gaps decrease in the series $S \rightarrow Se \rightarrow Te$ because of the rise in energy of the p states toward the vacuum level, i.e., CdS ($E_g = 2.42 \text{ eV}$), CdSe ($E_g = 1.74 \text{ eV}$) and CdTe ($E_g = 1.44 \text{ eV}$). [17] For similar reasons, the band gap drops from CuGaSe₂.($E_g =$ 1.68 eV) to CuInSe₂ (1.04 eV). [11] Hence, compounds exhibiting solid solubility of cations or anions provide a useful approach to finely adjust and set a band gap to a desired value, e.g., CuIn_{0.7}Ga_{0.3}Se₂ (~1.18 eV). [11] Chapters 3 and 4 provide excellent examples of using solid solutions to tune the optical and electrical properties of semiconductors. Among Fe chalcogenides, e.g. FeS_2 pyrite, has long been and continues to be of interest as a PV absorber. [18] In this material, Fe^{2+} bears an analogy to closed-shell Cu⁺ (d¹⁰) in that the filled t_{2g} set of Fe^{2+} (d⁶⁺) is also filled. In Chapter 2, I consider the properties and characteristics of Fe-based chalcogenides that must be met for their condsideration as solar absorber candidates.

Optical and electrical properties of materials can readily be anticipated and rationalized on the basis of a crystal structure. Piezoelectricity, ferroelectricity, and second-order non-linear optical behavior are properties commonly associated with non-centrosymmetric crystals. [19] In Chapter 5, describe a new quaternary wide band-gap sulfide CuZnPS₄. It crystallizes in a non-centrosymetric space group, and it exhibits a strong second-order optical response. In largely ionic, wide band-gap materials (> 3 eV), charges are highly localized and optical transitions are isolated on specific dopant atoms. In Chapter 6, I consider the fluoride YZrF₇ and its characteristics as a host for optical upconversion.

1.4 Upconversion process

The upconversion process [20-22] is converting near infrared (NIR) radiation into visible light. Rare-earth lanthanide ions e.g. Yb^{3+}/Er^{3+} or Yb^{3+}/Tm^{3+} in a proper host exhibit green and blue emission, respectively. Among of a variety of oxides and fluorides hosts, hexagonal NaYF₄ is known to show the highest upconversion luminescent efficiency with Yb/Er co-doping [22]. The design of compounds containing heavy elements could probably induce the low phonon energy and promise high upconversion efficiency by suppressing the non-radiative energy loss.

Recently, Down-conversion process [23, 24] has been proposed to optimize efficiency in Si and Si/Ge based solar cells. The luminescent material layers convert high photon energy in UV/visible range to NIR range absorbed effectively by Si and Ge. Similar approach could apply to upconversion process by utilizing lost photon energy in NIR range to be converted in visible range that absorbed by high band gap absorber.

1.5 Summary

Crystalline Si, CdTe and Cu(In, Ga)Se₂ represent the most common set of solar absorbers both under active study in the research community and in commercial use. The low absorption of crystalline Si, the toxicity of Cd, the rarity of In and Te, and the desire to make solar energy a significant world energy source encourage the researchers to identify, design, and develop new solar absorbers. The absorbers should contain earth abundant and non-toxic elements, and their absorption should be higher than Si, CdTe, and CIGS. The work presented in this dissertation, focused on synthesis, single-crystal structures, and optical and electrical properties, offers new insights for designing such materials, while also identifying promising candidate materials.

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Chapter 2

Ternary iron-based chalcogenide solar absorbers

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2.1 Introduction

Fool's gold, FeS₂ pyrite, has been of interest as a photovoltaic (PV) absorber for more than 20 years. Although it exhibits excellent optical and electrical properties, i.e., appropriate band gap (indirect 0.9-0.95 eV) [1, 2], high optical absorption ($\alpha > 10^5$ cm⁻¹ at Eg + 0.1 eV) [3], and high carrier mobility (about 300 cm²V⁻¹s⁻¹ in single crystals) [4], a viable open-circuit voltage has not been demonstrated. [2, 3] In thin films, it has also not been possible to suppress high carrier concentrations and sub-gap absorption. [5-7] Nowadays, PV research on inorganic-based absorbers is dominated by CdTe and Cu(In, Ga)Se₂ (CIGS) with the highest recorded efficiency of a CIGS cell at 20.3% [8]. Nevertheless, the scarcity of In and toxicity of Cd could limit the scaling of these materials to meaningful levels relative to world energy needs. New and efficient solar absorbers are crucial form improving solar-cell efficiency and expanding the reach of PV technologies.

Recently, coupled computational and experimental studies on pyrite thin films [7] have been used to identify the issues limiting pyrite performance. At the same time, design rules were proposed to guide the identification of new Fe-based solar abosrobers:

- A band gap of 1.3-1.4 eV is preferred on the basis of the Shockley-Quiesser model.

- Ternary Fe materials should not spontaneously phase separate into S deficient conducting materials having small band gaps. The defect calculation showed that S deficiency was difficult to form in bulk FeS₂, but simply created in FeS_{1-x} ($x \le 0.15$). Because of the low thermal stability of pyrite, decomposition of pyrite results in FeS_{1-x} ($x \le 0.15$) phases as impurities. These phases readily form as a thin layer on the surfaces of pyrite grains. They are the source of free carriers leading to absorption at energies below the band gap.

- Octahedral Fe²⁺ coordination. Chalcogenides containing tetrahedrally coordinated Fe²⁺ have small band gaps because of the small crystal filed (ligand field) splitting energy in a tetrahedral environment. For example, the band gap energy of CuFeS₂ chalcopyrite, a modified sphalerite-ZnS structure type, is only 0.6 eV [9].

In FeS₂ pyrite structure, Fe is coordinated by six S atoms in a distorted octahedral manner, while S is bound to three Fe atoms and one S atom comprising a distorted tetrahedral environment. Thus, pyrite structure resembles the NaCl rock salt structure with Fe and discrete S-S centers occupying the Na and Cl positions, respectively. With binary FeS₂ structure as a starting point, adding an additional element with strong covalent bonding to S should encourage stabilization of Fe²⁺ in an octahedral site. This concept led us to the ternary system [7] Fe₂MS₄ (M = Si, Ge) [7, 10]. In Fe₂MS₄, Fe²⁺ occupies half of the available octahedral sites, whereas M⁴⁺ occuipes 1/8 of the available tetrahedral sites. S²⁻ arrays are approximate hexagonal closed packing, thus Fe₂MS₄ is described as the olivine structure; a drawing of the crystal structure of Fe₂Ge(S, Se)₄ is given in Fig. 2.1.

This chapter is focused on the synthesis, and optical and electrical characterization of Fe_2GeS_4 single crystals and thin films. The solid solution series $Fe_2GeS_{4-x}Se_x$ ($0 \le x \le 4$) has also been included to examine tuning of the band gap.



Figure 2.1 Crystal structure of olivine Fe_2GeQ_4 (Q = S, Se) and coordination around Fe, Ge and Q centers.

2.2 Experimental

2.2.1 Sample preparation

Fe₂SiS₄, Fe₂GeS₄, Fe₂GeSe₄, and Fe₂GeS _{4-x}Se_x ($0 \le x \le 4$) powder samples were synthesized by solid state reaction of the corresponding elemental powder mixtures in evacuated, sealed fused silica tubes. Metal powder sources used in this work were Fe (Alfa Aesar, 99.998%), Si (Alfa Aesar, 99.9985%), Ge (Alfa Aesar, 99.999%), S (Cerac, 99.999%), and Se (Alfa Aesar, 99.999%). Synthesis conditions for each compound are listed in Table 2.1.

Compound	Fe ₂ SiS ₄	Fe ₂ GeS ₄	Fe ₂ GeSe ₄	Fe ₂ GeS _{4-x} Se _x
				(0 < x < 4)
Condition for	1000-1025°C,	600-700°C,	500°C,	500-600°C,
powder sample	72-96 h	48 h	48 h	48 h
Condition for	T1 = 1050°C,	T1 = 980°C,	-	$T1 = 900^{\circ}C,$
crystal growth	T2 = 1000°C,	$T2 = 940^{\circ}C,$		T2 = 800°C,
	T3 = 950°C	$T3 = 900^{\circ}C$		T3 = 700°C

Table 2.1 Synthesis condition of Fe_2SiS_4 , Fe_2GeS_4 , Fe_2GeSe_4 , and $Fe_2GeS_{4-x}Se_x$ ($0 \le x \le 4$).

Single crystals of Fe₂SiS₄ and Fe₂GeS₄ were grown by chemical vapor transport (CVT) using I₂ (Alfa Aesar, 99.99+%) as the transport agent (5 mg/cm³) [11]. Evacuated sealed silica tubes containing mixtures of elemental powders and transport agent were heated in a three-zone ATS series 3210 split tube furnace at 700 °C (24 h) for Fe₂GeS₄, 500 °C (24 h) for Fe₂GeS_{4-x}Se_x and 1000 °C (72h) for Fe₂SiS₄. Thermal gradients were programmed across the tubes as detailed in Table 2.1. The tubes were held at the initial point for 72h, cooled at a rate of 5°C/h to 400-500 °C, and then naturally cooled to room temperature by turning off power to the furnace. Black needle crystals from 1 to 10 mm in length (Fig. 2.2) were found at the cold zone of the tubes. The identity of the crystals as Fe₂GeS₄ was verified by determination of cell parameters via single-crystal X-ray

diffraction – ICSD #333. The Fe₂GeS_{4-x}Se_x and Fe₂SiS₄ crystals were smaller than Fe₂GeS₄ under the described growth conditions. The crystals were too small to perform optical and electrical measurements. However, this is the first report on Fe₂GeS_{4-x}Se_x and Fe₂SiS₄ single crystal growth via CVT method. The Fe₂SiS₄ crystals were characterized by single-crystal X-ray diffraction and found to have unit-cell similar to those previously reported - ICSD #332.



Figure 2.2 Fe₂GeS₄ as-grown single crystals by CVT method.

2.2.2 Phase characterization and structural refinement

X-ray Diffraction (XRD) data for powder samples were collected with a Rigaku Ultima IV Diffractometer, utilizing Cu K α radiation. Lattice parameters in solid solution powder samples were calculated by using PDXL software [12]. X-ray Diffraction data for single crystals were collected on a Bruker SMART APEX CCD diffractometer, utilizing Mo K α radiation. The space group was determined based on systematic absences. Absorption corrections were applied by SADABS [13]. The structures were solved by using direct methods and Fourier techniques and refined by full matrix least-squares procedure on F². All atoms were refined with anisotropic thermal parameters. All software and sources of scattering factors used in the calculations are contained in the SHELXTL 6.10 package [14].

2.2.3 Optical and Electrical measurements

Optical band gaps of powder sample were determined from diffuse reflectance data obtained from a spectrometer comprising an Ocean Optics HR4000 UV-VIS detector with a DH-2000-BAL balanced deuterium/tungsten halogen source. MgO powder (Cerac, 99.95%) was used as the reference. The reflectance spectra were converted to absorbance based on modification of the Kubelka-Munk theory [15, 16].

$$F(R) = (1 - R)^2/2R = k/s$$
 (Eq. 2.1)

where, R = reflectivity corrected from $R_{sample}/R_{standard}$, k = absorption coefficient

and s = scattering coefficient

Approximate optical band gaps were determined from k/s vs. E (eV) plots. For single crystal and thin-film samples, optical transmission and reflection were collected from the same system as described above. An absorption coefficient (α) was calculated from Eqs. 2.2 and 2.3 [17],

T = (1-R)
$$e^{-\alpha t}$$
 (Eq. 2.2)
thus, α = - [ln(T/1-R)]/t (Eq. 2.3)

where, T = transmission, R = reflection and t = thickness of sample

The thickness of crystals was measured by a high resolution optical microscope (Leica DMRM microscope). Room temperature 4-point resistivity was measured in the van der Pauw geometry on a Hall Measurement System from LakeShore 7504 using indium gold as metal contacts. Majority carrier type was determined from Seebeck measurements on a custom-built system.

2.2.4 Thin-film deposition of Fe₂GeS₄ and thermogravimetric analysis

A Fe₂GeS₄ thin film was prepared by using a solution spin-coating process. First, Fe-precursor films were depositing by spin coating an aqueous Fe(NO₃)₃·9H₂O (Alfa Aesar, ACS, 98.0-101.0%) solution onto a clean fused silica substrates by following a procedure previously reported. [18] The thickness of Fe-precursor film ~10 nm/coat. Second, Ge and S sources was sourced via a 0.25 M solution of GeS₂ in hydrazine
hydrate N₂H₄'H₂O (MP Biomedicals, 85%, ~54.4% N₂H₄). GeS₂ powder was synthesized by solid state reaction of Ge and S powder in an evacuated sealed tube for > 24h at 600°C. GeS₂ powder is easily dissolved in hydrazine hydrate, and the solution remains stable for 4-5 days in air. The solubility was found to increase upon addition of excess S powder. The GeS₂ solution was pass through a syringe filter (0.45 µm pore size) prior to use. 3-4 drops of GeS₂ solution was spun on ~50 nm Fe-precursor films at 3000 rpm for 30 s in air, before heating films on a hot plate at 130 °C for 1 min and 250 °C for 1 min with ramping rate 10 °C/min. The thickness of the GeS₂ layer was ~50 nm/coat. An Fe₂GeS₄ film was obtained by annealing the Fe-Ge-S precursor film in an evacuated sealed tube with 0.01-0.02 g of GeS₂ powder at 680 °C for 2 h.

An Fe_2GeS_4 film was also deposited via RF magnetron sputtering. The deposition details have been described previously. [7] Cross section images of Fe_2GeS_4 thin films were collected on a ZEISS Ultra-55 microscope. Thermogravimetric analysis was conducted with a Mettler Toledo TGA850 instrument by heating samples in alumina cups under flowing N₂ (g) at rate of 10^oC/min.

2.3 Results and Discussion

2.3.1 Phase characterization

As seen from the X-ray diffraction patterns in Figs. 2.3 and 2.4, essentially single phase Fe_2MS_4 (M = Si, Ge) powders and Fe_2GeS_4 thin films can readily be synthesized. In the solid-solution series $Fe_2GeS_{4-x}Se_x$ (0 ≤ x ≤ 4) (Fig. 2.5), the peak shifts to smaller 20 with increasing Se content is consistent with substitution of Se on the S sites. Lattice parameters (Fig. 2.6) and unit-cell volume (Fig. 2.7) correspondingly increase in a nearly linear manner. Alterations in the relative intensity ratios throughout the X-ray patterns match those in simulated patterns (Fig. 2.5).



Figure 2.3 Powder XRD patterns of Fe_2SiS_4 and Fe_2GeS_4 .



Figure 2.4 XRD pattern of Fe_2GeS_4 thin film by solution process.



Figure 2.5 (a) Experimental XRD patterns of $Fe_2GeS_{4-x}Se_x$ ($0 \le x \le 4$) (b) calculated patterns of Fe_2GeS_4 and Fe_2GeSe_4 .



Figure 2.6 Plot of a, b and c parameters of $Fe_2GeS_{4-x}Se_x$ ($0 \le x \le 4$).



Figure 2.7 Unit cell volume plot (black) and band gap approximation (blue) of Fe_2GeS_4 . _xSe_x (0 ≤ x ≤ 4).



Figure 2.8 TGA plot of $Fe_2(Si, Ge)S_4$ in comparison with FeS_2 pyrite.

2.3.2 Thermal stability

Results of thermogravimetric measurements for Fe₂SiS₄, Fe₂GeS₄, and FeS₂ are given in Fig. 2.8. Fe₂SiS₄ exhibits the highest thermal stability with decomposition occurring at ~1025 °C, while Fe₂GeS₄ begins to decompose at ~700 °C. The products following decomposition were characterized by XRD and found to be dominated by FeS. So, the thermal decomposition reaction of Fe₂(Si, Ge)S₄ is likely:

 $Fe_2(Si, Ge)S_4(s) \longrightarrow 2FeS(s) + (Si, Ge)S_2(g).$

 FeS_2 pyrite begins to decompose above 600 °C in inert atmosphere, whereas the mass loss occurred approximately 200 °C lower in the presence of oxygen. FeS was identified following decomposition in the inert atmosphere, while Fe_2O_3 phase was identified following heating in air. Clearly, oxidation occurs at much lower temperature that that of thermal decomposition.

Proposed thermal decomposition reaction:

$$FeS_2(s) \longrightarrow Fe_{1-x}S(s) + S_2(g)$$

Proposed oxidation reaction with oxygen:

$$2\text{FeS}_2(s) + 3.5\text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s) + 2\text{SO}_2(g)$$

In conclusion, $Fe_2(Si, Ge)S_4$ exhibits a much higher thermal stability than FeS_2 pyrite under an inert atmosphere. No further TGA data were collected for $Fe_2(Si, Ge)S_4$ under oxidizing atmosphere. Considering the oxophilic nature of Fe, Si, and Ge, it it presumed that oxidation will occur at much lower temperature than that of the decomposition.

2.3.3 Chemical vapor transport in Fe₂MS₄ system (M = Ge, Si)

Single-crystal growth of Fe_2GeS_4 by using the CVT method with I_2 as the transport agent has previously reported [11]. Proposed reactions for the system are shown below. At 500-700 °C: formation of binary compounds

$$Fe (s) + S(g) \longrightarrow FeS (s)$$

$$Ge (s) + 2S (g) \longrightarrow GeS_2 (s) \longrightarrow GeS_2 (g)$$

$$Ge (s) + I_2 (g) \longrightarrow GeI_4 (I, g)$$

$$Ge (s) + I_2 (g) \longrightarrow GeI_2 (I, g)$$

$$FeS (s) + GeS_2 (s, g) \longrightarrow Fe_2GeS_4 (s)$$

$$FeS (s) + I_2 (g) \longrightarrow FeI_2 (I) + S (g)$$

At 900-980 °C: transport

$$Fe_{2}GeS_{4} (s) \longrightarrow FeS (s) + GeS_{2} (g)$$

$$Fel_{2} (l) \longrightarrow Fel_{2} (g)$$

$$GeS_{2} (g) + l_{2} (g) \longrightarrow Gel_{4} (g) + S (g)$$

$$Fel_{2} (g) + GeS_{2} (g) \longrightarrow Fe_{2}GeS_{4} (s) + l_{2} (g)$$

Since Gel₄ and Gel₂ are unstable and decompose around 440-550 °C [19, 20] and GeS₂ vaporizes above 600 °C, Ge is expected to transport as the sulfide at high temperatures. FeS has a high melting point (1194°C) [20], so volatile species is needed for transport. Among the binary iron (II) halides [20]: Fel₂ (m.p. ~587 °C), FeBr₂ (m.p. ~684 °C) and FeCl₂ (m.p. ~677 °C), Fel₂ was found to have the lowest melting point with an associated boiling point of 935 °C [21], so I₂ was chosen as the transport agent. On cooling sample tubes, Fe₂GeS₄ crystal growth was observed with crystal size scaling inversely with cooling rate. Small amounts of FeS/Fe₇S₈ in the hot zone and GeS₂ in the Fe₂GeS₄ crystals.

Proposed reactions for Fe_2SiS_4 are similar to those of Fe_2GeS_4 , except at higher temperatures (>950 °C) are required to efficiently generate SiS₂. The growth conditions described in Table 2.1 were readily optimized to yield crystal of sufficient size for optical and electrical measurements

2.3.4 Optical and electrical characterization

Experimental band gap of $Fe_2(Si, Ge)S_4$ were first investigated in [18]. The similar result measured by diffuse reflectance technique is shown in Figs. 2.7 and 2.9, and found that Fe_2SiS_4 band gap is ~1.7 eV. In Fe_2GeS_4 , both powder and single crystal samples

showed band gap energy ~1.4 eV. The experimental band gap of both compounds agreed with calculated band gap; 1.55 eV for Fe₂SiS₄ and 1.36 eV for Fe₂GeS₄ [7]. The averaged band gap of Fe₂GeS_{4-x}Se_x ($0 \le x \le 4$) is demonstrated in Fig. 2.7. The Se substitution in Fe₂GeS_{4-x}Se_x decreased band gap energy from ~1.45 eV in x = 0 down to 0.6±0.1 eV when x = 4. The compositions with x = 0-2 yielded useful band gap for PV absorber.

A ~50 micron thickness of Fe₂GeS₄ single crystal is tried to measure transmission and reflection to determine absorption coefficient. The low transmission (< 20%) of very thick crystal resulted in signal cutting of at the above 1.5 eV (Fig. 2.10, line A) which was supposed to be the strong turning on of light absorption around the material's energy gap. The absorption coefficient could not be calculated in this single crystal, however, the band gap obtained from T and R measurements is ~1.4 eV in good agreement with calculated value. The calculation on absorption of Fe₂GeS₄ predicted α in range of 10⁵ cm⁻¹ [7]. Hence, appropriate sample's thickness is estimated to be able to allow enough light transmission through sample. Fig. 2.10, line B is a simulated absorption when applying sample's thickness to 0.5 µm based on the result of line A, so approximate thickness of Fe_2GeS_4 sample should be at least in range of 0.5 µm. An experimental absorption coefficient of Fe₂GeS₄ is measured from a thin-film sample (Fig. 2.10, line C) and displayed high absorption $\alpha > 10^5$ cm⁻¹ at h $\nu > 2$ eV in good agreement with the theoretical calculation. As a result of high absorption observed in this material, the thickness of crystal should be very thin and larger area than beam light; pretty difficult in practical way to mechanically polish a single crystal to obtain thickness in that range. Nano milling technique, such as Ion milling, Focused ion beam (FIB) milling, will leave a consideration for future improvement in the measurement technique.



Figure 2.9 Diffuse reflectance spectra of $Fe_2(Si, Ge)S_4$ samples.



Figure 2.10 Optical absorption of Fe₂GeS₄ single crystal.



Figure 2.11 Transmission T, reflection R, and reflection-corrected transmission T/1-R spectroscopy data of a ~100 nm of Fe_2GeS_4 thin film by solution processing.



Figure 2.12 Absorption of a ~100 nm Fe₂GeS₄ thin film by solution processing.

Fig. 2.11 and Fig. 2.12 demonstrated T, R and α of Fe₂GeS₄ thin film deposited by solution processing. Band gap and absorption coefficient is similar to those of the film deposited by sputtering method shown in Fig. 2.10. Nevertheless, the absorption onset below 1.5 eV (sub-gap absorption) is notably high in range of 10⁴ cm⁻¹. Since the spin-coating and film treatment, e.g. solvent evaporation, were performed under air, and the Fe-precursors before spin-coating GeS₂ solution was proposed to be FeO(OH) [18]. If the

reaction with GeS_2 did not fully converted FeO(OH) to Fe_2GeS_4 , the impurities, such as FeS, $Fe_{1-x}S$, Fe_2O_3 , could be existed and responsible to the sub-gap absorption.

Electrical resistivity of Fe_2GeS_4 single crystals are measured in range of 800-1200 Ω cm, where room temperature Seebeck coefficients are in range of +750 to +950 μ V/K indicating a characteristic of *p*-type semiconductor. *P*-type semiconducting behavior is still observed at low temperature upto 260 K (Fig. 2.13). Below 260 K, very high Seebeck coefficient and resistance showed an insulating behavior. Carrier concentration [22] of a Fe2GeS4 single crystal on basis of the resistivity and Seebeck coefficient data is estimated in range of 10¹⁸ cm⁻³.



Figure 2.13 Temperature dependent Seebeck coefficient of a Fe₂GeS₄ single crystal.

2.3.5 Crystal Structure of Fe₂GeS_{1.34}Se_{2.66}

Crystal structure of $Fe_2GeS_{4-x}Se_x$ solid-solution was studied via a single crystal structure refinement of Fe_2GeSSe_3 . The actual composition of S and Se is found to be 1.34 and 2.66, respectively. Crystallographic data of $Fe_2GeS_{1.36}Se_{2.66}$ is shown in Tables 2.2-2.4. Single crystal refinements use Fe_2GeS_4 [10] and Fe_2GeSe_4 [23] as model structures, thus the refined structure of the solid-solution is quite similar to its ternary

counterparts, i.e., olivine structure type, lattice parameters, bond lengths, and bond angles. A crystal structure drawing of Fe₂GeS_{1.36}Se_{2.66} is given in Fig. 2.1. It crystallizes in orthorhombic unit cell with space group Pnma (no. 62) consisting of distorted 6-fold coordinated [FeQ₆] units (Q = S, Se), 4-fold coordinated [GeQ₄] units, and approximately hexagonal closed packing of Q arrays. Connectivities between [Fe(1)Q₆]-[Fe(1)Q₆] and $[Fe(1)Q_6]$ - $[Fe(2)Q_6]$ are edge sharing, while $[Fe(2)Q_6]$ - $[Fe(2)Q_6]$ is corner sharing. Disordering of S and Se occupation is found on all three chalcogenide sites whose site occupation factors are: S(1)/Se(1) = 0.57/0.43, S(2)/Se(2) = 0.35/0.65, and S(3)/Se(3) = 0.21/0.79. Hence, the refined bond lengths and bond angles are averaged between Fe-S and Fe-Se bonding (same for Ge-S and Ge-Se bonding) for each site shown in Table 2.5, i.e., Fe(1)–Q(1) = 2.5351(6) Å, Fe(1)-Q(2) = 2.6093(5) Å, Fe(1)-Q(3) = 2.6389(5) Å, Fe(2)-Q(1) = 2.5915(13) Å, Fe(2)-Q(2) = 2.5207(11) Å, Fe(2)-Q(3) = 2.5753(7) Å and 2.7001(8) Å, Ge-Q(1) 2.2699(11) Å, Ge-Q(2) 2.3396(10) Å, and Ge-Q(3) 2.3515(6) Å. Slightly unequal bond distances in axial and equatorial plains of $[FeQ_6]$ and $[GeQ_4]$ could be associated with electrostatic repulsion between cations, i.e., the Fe-Q distances at the shared edge was longer than that of the unshared one. Weak Jahn-Teller distortion in octahedral d⁶-Fe²⁺ might be responsible as well. Fig. 2.14 showed an example of d⁶ high spin ions experiencing a Jahn-Teller distortion [24] causing a non-degeneracy of e_{a} and t_{2a} energy levels resulting in metal-ligand bonding along z-axis, either shorter or longer. Difference in Fe-Q(1), Fe-Q(2) and Fe-Q(3) distance causes bond angle deviation 2° to 6° from an ideal octahedral angle, where the distortion at Fe(2) centers is more than Fe(1). The distortion at Ge centers can be explained in similar fashion; deviated angles are up to 8° from an ideal tetrahedral angle. These distortions in Fe₂Ge(S, Se)₄ are found to be less than olivine type oxides [10] e.g. Fe₂SiO₄, Mg₂SiO₄ because of a nature of covalent bonding of Fe-S [10].

Formula weight	437.17
Wavelength	0.71073 Å
Crystal system and Space group	Orthorhombic, Pnma (No. 62)
Unit cell dimensions	a = 12.8851(15) Å, b = 7.4541(9) Å, c = 6.0919(7)
Å	
	$\alpha = \beta = \gamma = 90^{\circ}$
Volume	585.11(12) Å ³
Z	4
Density (calculated)	4.963 g/cm ³
Absorption coefficient	26.856 mm ⁻¹
F(000)	783
Crystal size	0.35 x 0.02 x 0.01 mm ³
Theta range for data collection	3.16 to 26.99°.
Index ranges	-16≤ h ≤16, -9≤ k ≤9, -7≤ l ≤7
Reflections collected	5922
Independent reflections	692 [R(int) = 0.0319]
Completeness to theta = 26.99°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7750 and 0.0382
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	692 / 2 / 46
Goodness-of-fit on F ²	1.163
Final R indices [I>2sigma(I)]	R1 = 0.0261, wR2 = 0.0559
R indices (all data)	R1 = 0.0312, wR2 = 0.0585
Extinction coefficient	0.0018(3)
Largest diff. peak and hole	0.650 and -0.837 e.Å ⁻³

Table 2.2 Crystal data and structure refinement for $Fe_2GeS_{1.34}Se_{2.66}$ at 293 K.

Atom	Site	х	у	Z	Occupancy	U(eq)
Fe(1)	4a	0	0	0	1	0.016(1)
Fe(2)	4c	0.2320(1)	0.2500	0.5029(1)	1	0.016(1)
Ge	4c	0.4129(1)	0.2500	0.0783(1)	1	0.011(1)
Se(1)	4c	0.4088(1)	0.2500	0.7058(2)	0.43	0.011(1)
S(1)	4c	0.4088(1)	0.2500	0.7058(2)	0.57	0.011(1)
Se(2)	4c	0.5761(1)	0.2500	0.2470(1)	0.65	0.012(1)
S(2)	4c	0.5761(1)	0.2500	0.2470(1)	0.35	0.012(1)
Se(3)	8d	0.3319(1)	0.0059	0.2527(1)	0.79	0.011(1)
S(3)	8d	0.3319(1)	0.0059	0.2527(1)	0.21	0.011(1)

Table 2.3 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$). U(eq) is defined as one third of the trace of the orthogonalized U_{ii} tensor.

Table 2.4 Anisotropic displacement parameters (Å²) for Fe₂GeS_{1.34}Se_{2.66}. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h²a^{*2}U¹¹ + ... + 2 h k a^{*} b^{*} U¹²]

	U11	U22	U33	U23	U13	U12	
 Fe(1)	0.018(1)	0.016(1)	0.013(1)	-0.002(1)	0.001(1)	0.001(1)	
Fe(2)	0.017(1)	0.018(1)	0.014(1)	0	0.002(1)	0	
Ge(4)	0.011(1)	0.012(1)	0.009(1)	0	0.000(1)	0	
Se(1)	0.013(1)	0.013(1)	0.007(1)	0	0.000(1)	0	
S(1)	0.013(1)	0.013(1)	0.007(1)	0	0.000(1)	0	
Se(2)	0.011(1)	0.013(1)	0.010(1)	0	0.001(1)	0	
S(2)	0.011(1)	0.013(1)	0.010(1)	0	0.001(1)	0	
Se(3)	0.013(1)	0.012(1)	0.010(1)	-0.001(1)	0.000(1)	-0.002(1)	
S(3)	0.013(1)	0.012(1)	0.010(1)	-0.001(1)	0.000(1)	-0.002(1)	

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,y,-z+1/2 #2 -x+1/2,-y,z-1/2 #3 -x+1/2,y+1/2,z+1/2

```
#7 x,y,z+1 #8 x+1/2,-y+1/2,-z+1/2 #9 x+1/2,y,-z+1/2
```

Table 2.5 Bond lengths (Å) and angles (degree) for $Fe_2GeS_{1.34}Se_{2.66}$.

Fe(1)-S(1)#1	2.5351(6)	Ge(4)-Se(1)#6	2.2699(11)
Fe(1)-Se(1)#2	2.5351(6)	Ge(4)-Se(2)	2.3396(10)
Fe(1)-Se(1)#1	2.5351(6)	Ge(4)-S(3)#5	2.3515(6)
Fe(1)-S(1)#2	2.5351(6)	Ge(4)-Se(3)	2.3515(6)
Fe(1)-S(2)#2	2.6093(5)	Ge(4)-Se(3)#5	2.3515(6)
Fe(1)-Se(2)#2	2.6093(5)	Se(1)-Ge(4)#7	2.2699(11)
Fe(1)-S(2)#1	2.6093(5)	Se(1)-Fe(1)#4	2.5351(6)
Fe(1)-Se(2)#1	2.6093(5)	Se(1)-Fe(1)#8	2.5351(6)
Fe(1)-S(3)#1	2.6389(5)	Se(2)-Fe(2)#9	2.5207(11)
Fe(1)-Se(3)#1	2.6389(5)	Se(2)-Fe(1)#8	2.6093(5)
Fe(1)-Se(3)#2	2.6389(5)	Se(2)-Fe(1)#4	2.6093(5)
Fe(1)-S(3)#2	2.6389(5)	Se(3)-Fe(2)#2	2.5753(7)
Fe(2)-S(2)#1	2.5207(11)	Se(3)-Fe(1)#4	2.6389(5)
Fe(2)-Se(2)#1	2.5207(11)		
Fe(2)-S(3)#3	2.5753(7)	S(1)#1-Fe(1)-Se(1)#2	180.00(5)
Fe(2)-Se(3)#3	2.5753(7)	S(1)#1-Fe(1)-Se(1)#1	0.00(4)
Fe(2)-S(3)#4	2.5753(7)	Se(1)#2-Fe(1)-Se(1)#1	180.00(4)
Fe(2)-Se(3)#4	2.5753(7)	S(1)#1-Fe(1)-S(1)#2	180.00(5)
Fe(2)-Se(1)	2.5915(13)	Se(1)#2-Fe(1)-S(1)#2	0.00(4)
Fe(2)-Se(3)	2.7001(8)	Se(1)#1-Fe(1)-S(1)#2	180.00(5)
Fe(2)-Se(3)#5	2.7001(8)	S(1)#1-Fe(1)-S(2)#2	93.37(2)
Fe(2)-S(3)#5	2.7001(8)	Se(1)#2-Fe(1)-S(2)#2	86.63(2)
Ge(4)-S(1)#6	2.2699(11)	Se(1)#1-Fe(1)-S(2)#2	93.37(2)

S(1)#2-Fe(1)-S(2)#2	86.63(2)	Se(1)#2-Fe(1)-Se(3)#1	96.36(2)
S(1)#1-Fe(1)-Se(2)#2	93.37(2)	Se(1)#1-Fe(1)-Se(3)#1	83.64(2)
Se(1)#2-Fe(1)-Se(2)#2	86.63(2)	S(1)#2-Fe(1)-Se(3)#1	96.36(2)
Se(1)#1-Fe(1)-Se(2)#2	93.37(2)	S(2)#2-Fe(1)-Se(3)#1	92.345(19)
S(1)#2-Fe(1)-Se(2)#2	86.63(2)	Se(2)#2-Fe(1)-Se(3)#1	92.345(19)
S(2)#2-Fe(1)-Se(2)#2	0.00(2)	S(2)#1-Fe(1)-Se(3)#1	87.655(19)
S(1)#1-Fe(1)-S(2)#1	86.63(2)	Se(2)#1-Fe(1)-Se(3)#1	87.655(19)
Se(1)#2-Fe(1)-S(2)#1	93.37(2)	S(3)#1-Fe(1)-Se(3)#1	0.000(12)
Se(1)#1-Fe(1)-S(2)#1	86.63(2)	S(1)#1-Fe(1)-Se(3)#2	96.36(2)
S(1)#2-Fe(1)-S(2)#1	93.37(2)	Se(1)#2-Fe(1)-Se(3)#2	83.64(2)
S(2)#2-Fe(1)-S(2)#1	180.00(2)	Se(1)#1-Fe(1)-Se(3)#2	96.36(2)
Se(2)#2-Fe(1)-S(2)#1	180.00(2)	S(1)#2-Fe(1)-Se(3)#2	83.64(2)
S(1)#1-Fe(1)-Se(2)#1	86.63(2)	S(2)#2-Fe(1)-Se(3)#2	87.655(19)
Se(1)#2-Fe(1)-Se(2)#1	93.37(2)	Se(2)#2-Fe(1)-Se(3)#2	87.655(19)
Se(1)#1-Fe(1)-Se(2)#1	86.63(2)	S(2)#1-Fe(1)-Se(3)#2	92.345(19)
S(1)#2-Fe(1)-Se(2)#1	93.37(2)	Se(2)#1-Fe(1)-Se(3)#2	92.345(19)
S(2)#2-Fe(1)-Se(2)#1	180.00(2)	S(3)#1-Fe(1)-Se(3)#2	180.000(12)
Se(2)#2-Fe(1)-Se(2)#1	180.00(2)	Se(3)#1-Fe(1)-Se(3)#2	180.000(12)
S(2)#1-Fe(1)-Se(2)#1	0.00(2)	S(1)#1-Fe(1)-S(3)#2	96.36(2)
S(1)#1-Fe(1)-S(3)#1	83.64(2)	Se(1)#2-Fe(1)-S(3)#2	83.64(2)
Se(1)#2-Fe(1)-S(3)#1	96.36(2)	Se(1)#1-Fe(1)-S(3)#2	96.36(2)
Se(1)#1-Fe(1)-S(3)#1	83.64(2)	S(1)#2-Fe(1)-S(3)#2	83.64(2)
S(1)#2-Fe(1)-S(3)#1	96.36(2)	S(2)#2-Fe(1)-S(3)#2	87.655(19)
S(2)#2-Fe(1)-S(3)#1	92.345(19)	Se(2)#2-Fe(1)-S(3)#2	87.655(19)
Se(2)#2-Fe(1)-S(3)#1	92.345(19)	S(2)#1-Fe(1)-S(3)#2	92.345(19)
S(2)#1-Fe(1)-S(3)#1	87.655(19)	Se(2)#1-Fe(1)-S(3)#2	92.345(19)
Se(2)#1-Fe(1)-S(3)#1	87.655(19)	S(3)#1-Fe(1)-S(3)#2	180.000(12)
S(1)#1-Fe(1)-Se(3)#1	83.64(2)	Se(3)#1-Fe(1)-S(3)#2	180.000(12)

Se(3)#2-Fe(1)-S(3)#2	0.000(12)	Se(1)-Fe(2)-Se(3)	81.38(3)
S(2)#1-Fe(2)-Se(2)#1	0.00(2)	S(2)#1-Fe(2)-Se(3)#5	92.24(3)
S(2)#1-Fe(2)-S(3)#3	95.87(3)	Se(2)#1-Fe(2)-Se(3)#5	92.24(3)
Se(2)#1-Fe(2)-S(3)#3	95.87(3)	S(3)#3-Fe(2)-Se(3)#5	89.240(12)
S(2)#1-Fe(2)-Se(3)#3	95.87(3)	Se(3)#3-Fe(2)-Se(3)#5	89.240(12)
Se(2)#1-Fe(2)-Se(3)#3	95.87(3)	S(3)#4-Fe(2)-Se(3)#5	170.07(4)
S(3)#3-Fe(2)-Se(3)#3	0.00(3)	Se(3)#4-Fe(2)-Se(3)#5	170.07(4)
S(2)#1-Fe(2)-S(3)#4	95.87(3)	Se(1)-Fe(2)-Se(3)#5	81.38(3)
Se(2)#1-Fe(2)-S(3)#4	95.87(3)	Se(3)-Fe(2)-Se(3)#5	84.72(3)
S(3)#3-Fe(2)-S(3)#4	95.60(3)	S(2)#1-Fe(2)-S(3)#5	92.24(3)
Se(3)#3-Fe(2)-S(3)#4	95.60(3)	Se(2)#1-Fe(2)-S(3)#5	92.24(3)
S(2)#1-Fe(2)-Se(3)#4	95.87(3)	S(3)#3-Fe(2)-S(3)#5	89.240(12)
Se(2)#1-Fe(2)-Se(3)#4	95.87(3)	Se(3)#3-Fe(2)-S(3)#5	89.240(12)
S(3)#3-Fe(2)-Se(3)#4	95.60(3)	S(3)#4-Fe(2)-S(3)#5	170.07(4)
Se(3)#3-Fe(2)-Se(3)#4	95.60(3)	Se(3)#4-Fe(2)-S(3)#5	170.07(4)
S(3)#4-Fe(2)-Se(3)#4	0.00(2)	Se(1)-Fe(2)-S(3)#5	81.38(3)
S(2)#1-Fe(2)-Se(1)	171.32(4)	Se(3)-Fe(2)-S(3)#5	84.72(3)
Se(2)#1-Fe(2)-Se(1)	171.32(4)	Se(3)#5-Fe(2)-S(3)#5	0.00(2)
S(3)#3-Fe(2)-Se(1)	89.94(3)	S(1)#6-Ge(4)-Se(1)#6	0.00(4)
Se(3)#3-Fe(2)-Se(1)	89.94(3)	S(1)#6-Ge(4)-Se(2)	117.42(4)
S(3)#4-Fe(2)-Se(1)	89.94(3)	Se(1)#6-Ge(4)-Se(2)	117.42(4)
Se(3)#4-Fe(2)-Se(1)	89.94(3)	S(1)#6-Ge(4)-S(3)#5	116.18(2)
S(2)#1-Fe(2)-Se(3)	92.24(3)	Se(1)#6-Ge(4)-S(3)#5	116.18(2)
Se(2)#1-Fe(2)-Se(3)	92.24(3)	Se(2)-Ge(4)-S(3)#5	101.56(2)
S(3)#3-Fe(2)-Se(3)	170.07(4)	S(1)#6-Ge(4)-Se(3)	116.18(2)
Se(3)#3-Fe(2)-Se(3)	170.07(4)	Se(1)#6-Ge(4)-Se(3)	116.18(2)
S(3)#4-Fe(2)-Se(3)	89.240(12)	Se(2)-Ge(4)-Se(3)	101.56(2)
Se(3)#4-Fe(2)-Se(3)	89.240(12)	S(3)#5-Ge(4)-Se(3)	101.37(3)

S(1)#6-Ge(4)-Se(3)#5	116.18(2)	Ge(4)-Se(2)-Fe(1)#8	85.53(2)
Se(1)#6-Ge(4)-Se(3)#5	116.18(2)	Fe(2)#9-Se(2)-Fe(1)#8	131.001(16)
Se(2)-Ge(4)-Se(3)#5	101.56(2)	Ge(4)-Se(2)-Fe(1)#4	85.53(2)
S(3)#5-Ge(4)-Se(3)#5	0.00(2)	Fe(2)#9-Se(2)-Fe(1)#4	131.001(16)
Se(3)-Ge(4)-Se(3)#5	101.37(3)	Fe(1)#8-Se(2)-Fe(1)#4	91.15(2)
Ge(4)#7-Se(1)-Fe(1)#4	118.90(3)	Ge(4)-Se(3)-Fe(2)#2	116.61(3)
Ge(4)#7-Se(1)-Fe(1)#8	118.90(3)	Ge(4)-Se(3)-Fe(1)#4	84.63(2)
Fe(1)#4-Se(1)-Fe(1)#8	94.63(3)	Fe(2)#2-Se(3)-Fe(1)#4	125.95(2)
Ge(4)#7-Se(1)-Fe(2)	119.84(4)	Ge(4)-Se(3)-Fe(2)	86.88(2)
Fe(1)#4-Se(1)-Fe(2)	99.90(3)	Fe(2)#2-Se(3)-Fe(2)	132.87(2)
Fe(1)#8-Se(1)-Fe(2)	99.90(3)	Fe(1)#4-Se(3)-Fe(2)	94.62(2)
Ge(4)-Se(2)-Fe(2)#9	116.78(4)		



octahedral field z-axis longer z-axis shorter

(a) (b) (c) (d)

Figure 2.14 Energy diagram of high spin d⁶ transition metal ion. (a) free ion (b) octahedral coordination (no distortion) (c) distorted octahedral with z-axis longer than the other four metal-ligand bonds (d) distorted octahedral with z-axis shorter than the other four metal-ligand bonds.

The $Fe_2GeS_{1.34}Se_{2.66}$ powder was made and demonstrated an XRD pattern in good agreement with a simulated pattern from the single crystal data (Fig. 2.15). Band gap of this stoichiometry measured by diffuse reflectance is found to be 0.8-0.85 eV.



Figure 2.15 Powder XRD pattern of $Fe_2GeS_{1.34}Se_{2.66}$: (a) Experimental pattern (b) Simulated pattern.

2.4 Summary

We studied and demonstrated Fe₂GeS₄ as a solar absorber material with optical band gap ~1.4 eV, high absorption coefficient in range of 10^5 cm⁻¹, *p*-type semiconducting, and estimated carrier concentration ~ 10^{18} cm⁻³. Those properties as well as continuous band gap tuning capability via S-Se solid-solution provide advantages and promising system to directing research and improvement of novel solar absorbers and PV technology. Future studies in a thin film deposition of Fe₂SiS₄ (E_g ~ 1.7 eV) and solid solution of Fe₂(Si,Ge)(S,Se)₄ can develop high efficiency earth-abundant, low cost thin-film solar cells.

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Chapter 3

Earth-abundant Cu-based chalcogenide semiconductors as photovoltaic absorbers

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3.1 Introduction

The development of efficient, thin-film photovoltaic (PV) absorbers based on earth-abundant materials is critical for enabling terawatt-scale adoption of solar electricity [1]. Currently, high-efficiency crystalline-Si technologies dominate the PV landscape [2, 3]. Although metallurgical-grade Si is inexpensive and earth abundant, the high production costs of monocrystalline and polycrystalline wafer-based cells constrains use [2, 3]. Alternatively, thin-film cells offer a route to substantially reduced costs. The modest PV efficiencies of representative technologies, e.g., CdTe and Cu(In,Ga)Se₂ (CIGS) [3, 4], however, coupled with the toxicity of Cd and the high costs of rare In and Te, have also limited large-scale deployment. Although recent progress has been made in the development of Cu₂ZnSnS₄ (CZTS) as a new absorber [5], deep trap states created by the substitution of Sn(II) on Zn(II) sites may well limit ultimate device efficiency and use [6].

To achieve widespread use of solar energy, a diversity of new absorber materials comprising earth-abundant elements and offering the potential for high efficiencies must be identified and developed. The magnitude of the absorption coefficient, shape of the absorption curve, and band gap are critical criteria for selecting such materials. In a recent report [7], we demonstrated with the HSE hybrid functional method that the absorption of the material Cu₃PSe₄ is comparable to that of CIS. From analysis via the method of spectroscopic-limited maximum efficiency [8], CuInSe₂ is reported to be among the top solar absorbers in terms of theoretical cell efficiency (> 25%). Because Cu3PSe4 exhibits a faster rise in absorption coefficient above threshold than CIS, it offers a unique opportunity to examine the use of much thinner films in a cell. To enrich our understanding of this material and its derivatives, we have investigated the solid-solution series Cu₃PS_{4-x} Se_x ($0 \le x \le 4$) as a means to tune band gaps and absorption properties. At the same time, we have assessed electrical properties relevant to the development of solar absorbers. We demonstrate here that these materials exhibit a unique combination of optical and electrical properties that of interest for both single and multiple-junction PV [9] as well as for solar-fuel generation [10].

3.2 Experimental

3.2.1 Powder synthesis and crystal growth

Powder samples of $Cu_3PS_{4-x}Se_x$ ($0 \le x \le 4$) were prepared by mixing and grinding stoichiometric amounts of the elemental powders Cu (99.999%, Alfa Aesar), P (99.999+%, Materion Advanced Chemicals), S (99.999%, Cerac), and Se (99.999%, Alfa Aesar), under an Ar (g) atmosphere. The samples were then sealed in evacuated fused silica tubes and heated at 480-600 °C for 24 h followed by an additional grinding and heating for 24 h at the same temperature. Pressed pellets were made by cold pressing 12.5-mm diameter disks at 2.5 to 3 tons, and then sintering at synthesis temperature for 3 h under 10,000 psi of Ar gas in a hot isostatic press (American Isostatic Presses, Inc. AIP6-30H). Final pellet densities were approximately 70% of theoretical values.

Single crystals were grown by chemical vapor transport (CVT) with NH₄Br (99.999%, Alfa Aesar) as the transport agent. The sample tubes, containing mixed elemental powders and the transport agent (1.5 mg cm⁻³ for Cu₃PSe₄ and 5 mg cm⁻³ for Cu₃PS_{4-x}Se_x), were uniformly heated in a three-zone ATS series 3210 split tube furnace at 500 °C for 12 h. Then, a temperature gradient was applied by setting temperatures to 550° C (zone 1), 600 °C (zone 2), and 700 °C (zone 3) for 3 days before cooling at a rate of 5°C h⁻¹ to 400 °C (zone 1), 450 °C (zone 2) and 500 °C (zone 3). The furnace power was then turned off and allowed to cool to room temperature. Black needle-shaped crystals were found at the cold zone of each tube.

3.2.2 Chemical Analysis

Compositional analyses of Cu_3PSe_4 single crystals were acquired on an electron microprobe (Cameca SX-50) equipped with four tunable wavelength dispersive spectrometers. Operating conditions comprised a 40° takeoff angle and 18-keV beam energy at a current of 20 nA and 10-µm diameter.

3.2.3 X-ray characterization

Powder X-ray diffraction data were collected with a Rigaku Ultima IV diffractometer by using Cu Kα radiation. Lattice parameters of powder samples were refined by the use of PDXL software [11]. X-ray diffraction data for single crystals were collected on a Bruker SMART APEX CCD diffractometer at 293 K using Mo Kα radiation. The structures were solved using direct methods and completed by subsequent difference Fourier syntheses and refinement by full matrix least-squares procedure on F². Absorption corrections were applied by using the computer program SADABS [12]. All atoms were refined with anisotropic thermal parameters. The software for solution and refinement and sources of scattering factors are contained in the SHELXTL 6.10 package [13]. Details of the data collection and structure refinement were provided in Table 3.1. Positional, equivalent isotropic displacement parameters, and occupancy factors were listed in Table 3.2. Anisotropic displacement parameters were represented in Table 3.3.

3.2.4 Optical and electrical measurements

Optical band gaps were determined from diffuse-reflectance measurements on pressed pellets. Light was directed onto the sample from a DH-2000-BAL balanced deuterium/tungsten halogen source and detected with an Ocean Optics HR4000 UV-VIS spectrometer; MgO powder (99.95%, Cerac) was used as a white reference. Room temperature resistivity and Hall mobility were measured with the same pellets by employing the van der Pauw geometry and a LakeShore 7504 measurement system. Majority-carrier type was determined from Seebeck measurements on an custom-built system by applying a 3 °C temperature gradient to the sample.

Empirical formula	$Cu_{3}PS_{1.89}Se_{2.11}$	Cu ₃ PS _{0.71} Se _{3.29}
Formula weight	448.82	504.16
Wavelength	0.71073 Å	0.71073 Å
Space group	Pmn2₁	Pmn2 ₁
Unit cell dimensions	a = 7.5034(5) Å	a = 7.6164(6) Å
	b = 6.4951(5) Å	b = 6.5945(6) Å
	c = 6.2174(4) Å	c = 6.3107(5) Å
	$\alpha = \beta = \gamma = 90^{\circ}$	$\alpha = \beta = \gamma = 90^{\circ}$
Volume	303.01(4) Å ³	316.96(5) Å ³
Z	2	2
Density (calculated)	4.916 g/cm ³	5.282 g/cm ³
Absorption coefficient	23.88 mm ⁻¹	29.20 mm ⁻¹
F(000)	408	450
Theta range for data collection	1.63 to 27.00°	1.64 to 27.00°
Index ranges	$-9 \le h \le 9, -8 \le k \le 8,$	$-9 \le h \le 9, -8 \le k \le 8,$
	-7 ≤ ≤7	-8 ≤ I ≤8
Reflections collected	3248	3387
Independent reflections	710 [R(int) = 0.0224]	743 [R(int) = 0.0267]
Max. and min. transmission	0.0438 and 0.6470	0.0462 and 0.658
Data / restraints / parameters	710 / 3 / 49	743 / 3 / 50
Goodness-of-fit on F ²	1.048	1.000
Final R indices [I>2sigma(I)]	R1 = 0.0242,	R1 = 0.0283,
	wR2 = 0.0574	wR2 = 0.0660
R indices (all data)	R1 = 0.0252, wR2 = 0.0582	R1 = 0.0294, wR2 = 0.0678

 Table 3.1 Crystallographic data and details of X-ray diffraction for single crystals of solid

 solution at 293 K.

Table 3.2 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) of Cu₃PS_{1.89}Se_{2.11} and Cu₃PS_{0.71}Se_{3.29}. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Wyckoff sites	х	У	Z	U	Occupancy
	C	043PS1.89Se2.	11		
2a	0	0.6427(1)	0.0956(2)	0.026(1)	1
4b	0.7461(1)	0.1833(1)	0.0896(1)	0.026(1)	1
2a	0	0.3253(2)	0.5964(3)	0.008(1)	1
2a	0	0.3162(2)	0.2503(2)	0.013(1)	0.64
2a	0	0.3162(2)	0.2503(2)	0.013(1)	0.36
2a	0	0.6355(2)	0.7184(2)	0.013(1)	0.57
2a	0	0.6355(2)	0.7184(2)	0.013(1)	0.43
4b	0.7392(1)	0.8346(1)	0.2121(1)	0.013(1)	0.34
4b	0.7392(1)	0.8346(1)	0.2121(1)	0.013(1)	0.66
	C	Cu ₃ PS _{0.71} Se _{3.2}	29		
2a	0	0.6448(2)	0.0984(2)	0.025(1)	1
4b	0.7453(1)	0.1822(1)	0.0890(1)	0.024(1)	1
2a	0	0.3254(3)	0.5979(4)	0.09(1)	1
2a	0	0.3161(2)	0.2481(2)	0.013(1)	0.28
2a	0	0.3161(2)	0.2481(2)	0.013(1)	0.72
2a	0	0.6371(2)	0.7205(2)	0.013(1)	0.25
2a	0	0.6371(2)	0.7205(2)	0.013(1)	0.75
4b	0.7391(1)	0.8350(1)	0.2126(1)	0.013(1)	0.09
4b	0.7391(1)	0.8350(1)	0.2126(1)	0.013(1)	0.91
	Wyckoff sites 2a 4b 2a 2a 2a 2a 4b 4b 4b 2a 2a 4b 2a 2a 2a 2a 2a 2a 2a 2a 2a 2a 2a 2a 2a	Wyckoff sites x 2a 0 2a 0.7461(1) 2a 0 4b 0.7392(1) 2a 0 2a 0 <td>Wyckoff sitesxysites$UUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUU$</td> <td>Wyckoff sites x y Z 2ites Cu3PS1.89Se2.11 2a 0 0.6427(1) 0.0956(2) 4b 0.7461(1) 0.1833(1) 0.0896(1) 2a 0 0.3253(2) 0.5964(3) 2a 0 0.3162(2) 0.2503(2) 2a 0 0.3162(2) 0.2503(2) 2a 0 0.6355(2) 0.7184(2) 4b 0.7392(1) 0.8346(1) 0.2121(1) 4b 0.7392(1) 0.8346(1) 0.2121(1) 4b 0.7453(1) 0.1822(1) 0.0984(2) 4b 0.7453(1) 0.1822(1) 0.0890(1) 2a 0 0.3161(2) 0.2481(2) 2a 0 0.3161(2) 0.2481(2) 2a</td> <td>Wyckoff sitesxyZUsites$CU_3PS_{1,89}Se_{2,11}$2a00.6427(1)0.0956(2)0.026(1)4b0.7461(1)0.1833(1)0.0896(1)0.026(1)2a00.3253(2)0.5964(3)0.008(1)2a00.3162(2)0.2503(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)4b0.7392(1)0.8346(1)0.2121(1)0.013(1)4b0.7392(1)0.8346(1)0.2121(1)0.013(1)4b0.7453(1)0.1822(1)0.0984(2)0.025(1)4b0.7453(1)0.1822(1)0.0984(2)0.024(1)2a00.3161(2)0.2481(2)0.013(1)2a00.3161(2)0.2481(2)0.013(1)2a00.6371(2)0.7205(2)0.013(1)2a00.6371(2)0.7205(2)0.013(1)2a00.6371(2)0.7205(2)0.013(1)2a00.6371(2)0.2126(1)0.013(1)4b0.7391(1)0.8350(1)0.2126(1)0.013(1)</td>	Wyckoff sitesxysites $UUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUUU$	Wyckoff sites x y Z 2ites Cu3PS1.89Se2.11 2a 0 0.6427(1) 0.0956(2) 4b 0.7461(1) 0.1833(1) 0.0896(1) 2a 0 0.3253(2) 0.5964(3) 2a 0 0.3162(2) 0.2503(2) 2a 0 0.3162(2) 0.2503(2) 2a 0 0.6355(2) 0.7184(2) 4b 0.7392(1) 0.8346(1) 0.2121(1) 4b 0.7392(1) 0.8346(1) 0.2121(1) 4b 0.7453(1) 0.1822(1) 0.0984(2) 4b 0.7453(1) 0.1822(1) 0.0890(1) 2a 0 0.3161(2) 0.2481(2) 2a 0 0.3161(2) 0.2481(2) 2a	Wyckoff sitesxyZUsites $CU_3PS_{1,89}Se_{2,11}$ 2a00.6427(1)0.0956(2)0.026(1)4b0.7461(1)0.1833(1)0.0896(1)0.026(1)2a00.3253(2)0.5964(3)0.008(1)2a00.3162(2)0.2503(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)2a00.6355(2)0.7184(2)0.013(1)4b0.7392(1)0.8346(1)0.2121(1)0.013(1)4b0.7392(1)0.8346(1)0.2121(1)0.013(1)4b0.7453(1)0.1822(1)0.0984(2)0.025(1)4b0.7453(1)0.1822(1)0.0984(2)0.024(1)2a00.3161(2)0.2481(2)0.013(1)2a00.3161(2)0.2481(2)0.013(1)2a00.6371(2)0.7205(2)0.013(1)2a00.6371(2)0.7205(2)0.013(1)2a00.6371(2)0.7205(2)0.013(1)2a00.6371(2)0.2126(1)0.013(1)4b0.7391(1)0.8350(1)0.2126(1)0.013(1)

Table 3.3 Anisotropic displacement parameters $(Å^2 x \ 10^3)$ for $Cu_3PS_{1.89}Se_{2.11}$ and $Cu_3PS_{0.71}Se_{3.29}$ (Q = S, Se). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

Atom	U^{11}	U^{22}	U ³³	U ²³	U ¹³	U ¹²	
Cu ₃ PS _{1.89} Se _{2.11}							
Cu (1)	29(1)	25(1)	24(1)	2(1)	0	0	
Cu (2)	27(1)	27(1)	23(1)	-1(1)	-1(1)	-1(1)	
Ρ	8(1)	8(1)	8(1)	1(1)	0	0	
S (1)	13(1)	16(1)	10(1)	0(1)	0	0	
Se (1)	13(1)	16(1)	10(1)	0(1)	0	0	
S (2)	15(1)	12(1)	13(1)	-1(1)	0	0	
Se (2)	15(1)	12(1)	13(1)	-1(1)	0	0	
S (3)	12(1)	13(1)	13(1)	0(1)	-1(1)	-2(1)	
Se (3)	12(1)	13(1)	13(1)	0(1)	-1(1)	-2(1)	
		C	Cu ₃ PS _{0.71} Se	3.29			
Cu (1)	28(1)	25(1)	22(1)	3(1)	0	0	
Cu (2)	28(1)	26(1)	20(1)	-1(1)	0(1)	-1(1)	
Ρ	10(1)	11(1)	6(1)	1(1)	0	0	
S (1)	13(1)	17(1)	9(1)	0(1)	0	0	
Se (1)	13(1)	17(1)	9(1)	0(1)	0	0	
S (2)	15(1)	12(1)	13(1)	-1(1)	0	0	
Se (2)	15(1)	12(1)	13(1)	-1(1)	0	0	
S (3)	12(1)	13(1)	14(1)	0(1)	-1(1)	-2(1)	
Se (3)	12(1)	13(1)	14(1)	0(1)	-1(1)	-2(1)	

3.2.5. Photoelectrochemical (PEC) measurement

Cu₃PSe₄ single crystals were prepared as electrodes by first embedding the crystals in mounting wax and forming a back contact by evaporating a 20-nm thick film of Au (99.99%, gold coin). The contacted crystals were attached to tinned copper wire using silver epoxy (Epotech H20C). The wax was then melted and the crystals were removed and washed with acetone. Electrodes were completed by threading the wires through glass tubes and sealing the edges of the sample to the tube with non-conductive epoxy. Electrode surface areas ranged from 0.1 mm² to 0.8 mm² depending on the size of the crystals. The area of the electrode was measured using digitally scanned images with the ImageJ analysis package. Rectifying contacts were made to Cu₃PSe₄ by immersing it in an electrolyte consisting of 1 mM cobaltocenium hexafluorophosphate (98%, Strem chemicals), 0.2 mM cobaltocene in dry acetonitrile, and 0.25 M tetrabutylammonium hexafluorophosphate (>99%, Fluka, electrochemical grade) [14]. Cobaltocenium hexafluorophosphate was recrystallized from acetonitrile/diethyl ether and dried en vacuo overnight before use. Cobaltocene was generated inside the cell by electrochemical reduction of cobaltocenium hexafluorophosphate using Pt as the cathode and Pt behind a 4-mm vycor frit as the anode. Acetonitrile (100%, Mallinckrodt Chemicals) was taken from a solvent purification system and stored over 3 Å molecular sieves. All chemicals were stored in an inert atmosphere glovebox. Measurements were made inside the box using a standard three-electrode cell configuration. The Cu₃PSe₄ working electrode potential was referenced to a Pt wire poised at the solution potential and separated from the working electrode by ~ 2 mm. Pt mesh was used as the counter electrode. Open-circuit voltage $(V_{\alpha c})$, short-circuit current density (J_{sc}) , and current density-potential (J-E) measurements were performed using a potentiostat (Biologic SP-200). 100 mW cm⁻² of 660 nm light was provided by an LED (Thor Labs LEDD1B, M660L2) that was chopped using a function generator. The light intensity was calibrated by measuring the current produced under illumination of a silicon photodiode (UDT Sensors, Inc. UV-005) of known spectral responsivity that was placed in the cell at the same location as the photoelectrode.

3.3 Results and Discussion

3.3.1. Phase characterization

Powder X-Ray diffraction patterns for $Cu_3PS_{4-x}Se_x$ ($0 \le x \le 4$) are shown in Fig. 3.1. The experimental Cu_3PS_4 and Cu_3PSe_4 patterns are similar to those calculated from previously reported crystal structures [15, 16]. Intermediate compositions exhibit peak positions between those of Cu_3PS_4 and Cu_3PSe_4 . They are shifted to smaller two-theta angles as x increases, which is consistent with the substitution of Se for S and an expansion of the unit cell (Fig. 3.2).



Fig. 3.1 X-Ray diffraction patterns for Cu₃PS_{4-x}Se_x.



Fig. 3.2 Unit-cell volume for Cu₃PS_{4-x}Se_x.

Unit-cell parameters increase linearly across the solid-solution series. Cell parameters can be calculated from the following relationships derived from lattice parameter plots (Fig. 3.3):

a = 0.102x + 7.293	(Eq. 3.1)
b = 0.082x + 6.334	(Eq. 3.2)
c = 0.076x + 6.069	(Eq. 3.3)



Fig. 3.3 Lattice parameters and cell volume plot of Cu₃PS_{4-x} Se_x.



Fig. 3.4 (a) Crystal structure of $Cu_3P(S,Se)_4$, where Q = S, Se. (b) The tetrahedral coordination of Cu(1), Cu(2) and P.

3.3.2. Crystal structure of Cu₃PS_{1.89} Se_{2.11} and Cu₃PS_{0.71}Se_{3.29}

The crystal structure of Cu_3PSe_4 was first reported by Garin and Parthé [17], and later refined and corrected [16, 18]. It crystallizes in the enargite structure, space group $Pmn2_1$, similar to Cu_3PS_4 and Cu_3AsS_4 [15]. The structure may be considered to be a derivative of wurtzite with Cu and P ordered across tetrahedral interstices within the distorted close packing of S(Se) atoms (Fig. 3.4). The structure has been confirmed to be adopted by the two compositions $Cu_3PS_{1.89}Se_{2.11}$ and $Cu_3PS_{0.71}Se_{3.29}$.

Crystallographically, the structure is defined by two distinct Cu sites, one P site, and three Q = S, Se sites. As seen from consideration of the occupation of the occupation factors in Table 3.2, the S and Se atoms are not randomly distributed across the three Q sites. In both structures Se prefers occupation of the 4b site. The bond length of Cu-Q and P-Q (Q = S, Se) in the solid solutions fall between those of Cu₃PS₄ and Cu₃PSe₄, *cf.*, Table 3.4. The angular distortions of the CuQ₄ and PQ₄ tetrahedra are rather modest, i.e., Q-Cu-Q ranges from 103.50(4) to 114.39(5)^o and Q-P-Q ranges from 108.17 to 112.22(10)^o. The increase of Cu-Q and P-Q distances from Cu₃PS₄ to Cu₃PSe₄ are small, and does not significantly affect the Q-Cu-Q and Q-P-Q angles bond angles (Table 3.5).

Table 3.4 Selected bond length of Cu-Q and P-Q (Q = S, Se) in $Cu_3PS_{1.89}Se_{2.11}$ and $Cu_3PS_{0.71}Se_{3.29}$ comparison to Cu_3PS_4 [15] and Cu_3PSe_4 [16].

Crystal	Cu-Q (Å)	P-Q (Å)
$Cu_3PS_{1.89}Se_{2.11}$	2.318-2.431	2.153-2.195
$Cu_{3}PS_{0.71}Se_{3.29}$	2.356-2.458	2.196-2.227
Cu_3PS_4	2.297-2.368	2.059-2.075
Cu_3PSe_4	2.392-2.471	2.228-2.242

	$Cu_{3}PS_{1.89}Se_{2.11}$	$Cu_3PS_{0.71}Se_{3.29}$
Q(1)-Cu(1)-Q(2)	113.25(6)	112.34(6)
Q(1)-Cu(1)-Q(3)	110.12(3)	110.53(4)
Q(2)-Cu(1)-Q(3)	107.94(4)	107.70(4)
Q(3)-Cu(1)-Q(3)	107.26(5)	107.88(6)
Q(1)-Cu(2)-Q(2)	108.37(4)	108.18(4)
Q(1)-Cu(2)-Q(3)	114.20(4),	113.70(4),
	103.51(4)	103.50(4)
Q(2)-Cu(2)-Q(3)	113.88(4),	114.39(5),
	110.57(4)	110.38(4)
Q(3)-Cu(2)-Q(3)	105.77(3)	106.11(3)
Q(1)-P-Q(2)	112.21(9)	112.22(10)
Q(1)-P-Q(3)	108.35(6)	108.17(8)
Q(2)-P-Q(3)	109.11(6)	109.27(9)
Q(3)-P-Q(3)	109.70(8)	109.73(10)

Table 3.5 Selected bond angles (°) for $Cu_3PS_{1.89}Se_{2.11}$ and $Cu_3PS_{0.71}Se_{3.29}$ (Q = S, Se).

3.3.3. Optical characterization

Optical band gaps obtained from diffuse reflectance measurements for the $Cu_3PS_{4-x}Se_x$ series are shown in Fig. 3.5. The band gaps of Cu_3PSe_4 and Cu_3PS_4 are found to be 1.35 eV and 2.36 eV, respectively. Intermediate compositions with x = 1, 2, 3 exhibit absorption onsets near 1.5, 1.7, and 1.95 eV, respectively, demonstrating optical band gaps can be continuously tuned across the series. Our results are in good agreement with the reported experimental values for Cu_3PS_4 (2.38 eV) and Cu_3PS_3Se (2.06 eV) by Marzick et al. [19]

The observed trend of a decreasing band gap with increasing Se content is commonly observed, i.e., $CulnS_2$ (1.5 eV), $CulnSe_2$ (1.04 eV). In particular, electronic structure calculations [7] establish P 4s – S, Se *np* antibonding character near the

conduction band minimum (CBM) and Cu 3d – S, Se np bonding character near the valence band maximum (VBM) in Cu₃PS_{4-x}Se_x. The higher absolute energy level of Se 4p states compared to those of S 3p states raises the energy of the VBM, while the modest splitting of bonding and antibonding states for the Cu-Se and P-Se interacions *vs.* Cu-S and P-S interactions, repectively, leads to a lowerenergy CBM. The net effect is an overall narrowing of the energy gap in the materials with increasing Se concentration.

The direct gaps of Cu_3PSSe_3 (1.50 eV) and Cu_3PSe_4 (1.35 eV) are well suited for PV applications. When x is between 0 and 2, the $Cu_3PS_{4-x}Se_x$ has band gaps between 1.7 and 2.36 eV which are suitable for photoelectrochemical water-splitting applications [10, 20] or for use as an absorber layer in the top cell of a thin-film tandem PV device [9].



Fig. 3.5 Optical band gaps for Cu₃PS_{4-x}Se_x.

3.3.4. Electrical characterization

Resistivity, Hall, and Seebeck data from measurements on pressed pellets are summarized in Table 3.6. All samples exhibit positive Seebeck coefficients consistent with *p*-type semiconductor behavior and the prevalence of d^{10} Cu¹⁺ in the materials. Hole carrier concentrations derived from Hall coefficients fall in the range 10^{16} - 10^{17} cm⁻³, consistent with the magnitude of the Seebeck coefficients.

A decrease in resistivity is observed with increasing Se content between Cu_3PS_4 (x = 0) and Cu_3PSe_4 (x = 4). This enhanced conductivity was accompanied by a notable increase in hole mobility. The result was consistent with the high covalency of Cu-Se bonding and band broadening, which facilitated delocalization of charged carriers and high hole mobility. Typically, Hall mobility is difficult to measure on pressed bulk pellets because of grain-boundary-inhibited transport associated with a polycrystalline microstructure [21]. Limited densification can exacerbate issue in making meaningful electrical measurements. Hence, with pellet densities near only 70% of theoretical values, it is somewhat surprising that mobilities were easily measured. The measured Hall mobility, 13 cm² V⁻¹ s⁻¹, of polycrystalline bulk Cu₃PSe₄ is comparable to the value, 20 cm² V⁻¹ s⁻¹, reported for single crystals [22]. Clearly, the surfaces of the materials are rather benign with respect to scattering charge carriers – a notable feature for identifying candidate polycrystalline PV absrobers. Similar hole mobility, (3-22 cm² V⁻¹ s⁻¹) has been reported for single crystals of Cu(In, Ga)Se₂ [23].

The observed hole concentrations in the Cu₃P(S, Se)₄ materials are relatively low compared with many other Cu-based chalcogenides (typically >10¹⁸ cm⁻³), e.g., LaCuOS [24], BaCu₂S₂ [25], BaCuSeF [26], BaCuTeF [26], and Cu₃TaS₄.[26]. Each of these materials contains an electropositive element, e.g., La, Ba, Ta, with a relatively small atomic solid-state energy [27]. The ionic character of the bonding of these elements with S and Se is expected to push the absolute energy of the VBM closer to the vacuum level in comparison with the VBM of Cu₃P(S,Se)₄. This energy positioning will favor low formation energies for Cu vacancies, giving rise to high hole concentrations. In a more covalent compound, such as Cu₃PS_{4-x}Se_x, enhanced covalency arises from the P-S and P-Se interactions, contributing to deeper VBM and higher Cu vacancy formation energies. These characteristics are expected to lead to reduced hole concentrations and also higher mobilities because of reduced ionized impurity scattering.

х	Resisitivity	Seebeck	Carrier	Mobility
	(Ω cm)	coefficient	concentration	$(\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})$
		(µV K⁻¹)	(cm ⁻³)	
0	933	+674	-	-
1	494	+585	1.0 x 10 ¹⁶	1.0
2	189	+615	1.8 x10 ¹⁶	2.0
3	25	+590	4.0 x 10 ¹⁶	6.5
4	0.62	+360	5.8 x 10 ¹⁷	13.0

Table 3.6 Electrical properties of $Cu_3PS_{4-x}Se_x$ ($0 \le x \le 4$) pellets.

3.3.5. Photoelectrochemical (PEC) measurements

A PEC test cell with a Cu₃PSe₄ single crystal was used to assess initial PV device parameters, including short-circuit current density (J_{sc}) and open-circuit voltage (V_{cc}), without fabricating complete solid state PV devices which would require heterojunction development and top-contact optimization. Fig. 3.6 and Fig. 3.7b, show the open-circuit photovoltage and short-circuit photocurrent generated upon chopped illumination. The differences between the light and dark response yielded $V_{oc} \sim 0.12$ V and $J_{sc} \sim 0.25$ mA cm⁻², and also confirmed the Cu₃PSe₄ samples are *p*-type based on the sign of the photoresponse. The non-vertical portions of the J_{sc} curve as well as the hysteresis in the (J-*E*) response suggest that surface redox processes, likely associated with Cu, occur upon potential cycling. It is possibly associated with anodic discharge by migration of Cu ions through the semiconductor-liquid interface reported in the cells [20]. A non-chopped J-*E* curve in Fig. 3.7a was measured in order to estimate the overall energy conversion efficiency (η) ~ 0.02% and fill factor (*ff*) ~ 0.25, with similar J_{sc} and V_{oc} values as obtained under chopped illumination (Fig. 3.7b).



Fig. 3.6 PEC measurement of a Cu_3PSe_4 single crystal under 100 mW cm⁻² a chopped 660 nm light source: (a) Working electrode potential measured under open-circuit (the difference between the dark and light electrode potential is the V_{OC}) (b) Current density at 0 V vs E_{sol} (analogous to a J_{SC} measurement for a solid-state device). The small dark current measured at 0 V vs. E_{sol} is attributed to surface electrochemical reactions.


Fig. 3.7 Current density – Potential (J-*E*) curves collected using a Cu_3PSe_4 single-crystal electrode. (a) Dark and light (100 mW cm⁻² 660 nm) steady-state measurements collected at a scan rate of 20 mV s⁻¹. (b) Data collected using chopped light under similar conditions, sweeping from negative to positive potentials.

%Atomic (%)			Atomic ratio				
Cu	Р	Se	0	Br	Cu/P	Cu/Se	P/Se
37.5	12.5	50.0	-	-	3.00	0.75	0.25
36.8	12.6	49.5	1.05	0.0478	2.92	0.75	0.26
±0.1	±0.2	±0.2	±0.3	±0.016	±0.06	±0.01	±0.01
	Cu 37.5 36.8 ±0.1	%Atom Cu P 37.5 12.5 36.8 12.6 ±0.1 ±0.2	%Atomic (%) Cu P Se 37.5 12.5 50.0 36.8 12.6 49.5 ±0.1 ±0.2 ±0.2	%Atomic (%) Cu P Se O 37.5 12.5 50.0 - 36.8 12.6 49.5 1.05 ±0.1 ±0.2 ±0.2 ±0.3	%Atomic (%) Cu P Se O Br 37.5 12.5 50.0 - - 36.8 12.6 49.5 1.05 0.0478 ±0.1 ±0.2 ±0.2 ±0.3 ±0.016	%Atomic (%) Atomi Cu P Se O Br Cu/P 37.5 12.5 50.0 - - 3.00 36.8 12.6 49.5 1.05 0.0478 2.92 ±0.1 ±0.2 ±0.2 ±0.3 ±0.016 ±0.06	%Atomic (%) Atomic ratio Cu P Se O Br Cu/P Cu/Se 37.5 12.5 50.0 - - 3.00 0.75 36.8 12.6 49.5 1.05 0.0478 2.92 0.75 ±0.1 ±0.2 ±0.2 ±0.3 ±0.016 ±0.06 ±0.01

Table 3.7 Electron probe microanalysis (EPMA) assessment of Cu₃PSe₄ single crystals.

Electron probe microanalysis (EPMA, Table 3.7) shows that the Cu₃PSe₄ single crystals used as photoelectrodes contained small amounts of O and Br, possibly from the crystal-growth process. Oxidation of surfaces could act as barriers at the Cu₃PSe₄ single crystal surface. Halogen substitution on anion sites from the bromide flux during CVT growth could act as compensating *n*-type dopants that would decrease the hole concentration and mobility. EPMA indicated P-excess in the single crystals could be the signature of the above discussed compensated defects that further inhibit hole mobility. These effects may play an important role in limiting the observed the PEC response. The small size (< 1 mm) of the single crystals prevented their further characterization by Hall or resistivity measurements. The pressed polycrystalline pellets also showed *p*-type photoresponse during PEC evaluation, although with much smaller magnitude than the single crystals and with a larger hysteresis. This may be related to the porosity of the pressed pellets or to grain boundaries. Further studies to control the doping as well as treatments to control surface chemistry are needed to improve the response.

3.4 Summary

The materials $Cu_3PS_{4-x}Se_x$ ($0 \le x \le 4$) comprise a solid-solution series of *p*-type semiconductors containing earth-abundant elements. They are found to exhibit continuously tuneable band gaps ranging from 2.36 eV (x = 0) to 1.35 eV (x = 4), hole

concentrations from ~ 10^{16} - 10^{17} cm⁻³, and hole mobilities from 1-13 cm² V⁻¹ s⁻¹, are relatively high. Initial photoelectrochemical studies on single crystals of Cu₃PSe₄ demonstrated photovoltages of 0.12 V and short circuit currents of 0.25 mA cm⁻² under 100 mW cm⁻² of 660 nm illumination. The observation of promising semiconductor properties and photoelectrochemical response in these materials provides an important first-step toward the development as PV absorbers. Their tunable band gaps provide unique opportunities for addressing needs in single and multijunction cells for both PV and photoelectrochemical water splitting with a single absorber materials set.

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Synthesis and characterization of $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$)

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4.1 Introduction

In a conventional single junction solar cell, photons having energy higher than the cell's band gap (E_a of solar absorber material) have their excess energy lost as heat, while photon energy below the band gap of material are not absorbed, and eventually again lost. Multijunction solar cell concept [1, 2] provides an effective approach to utilize those lost energy, by dividing up a spectrum into several spectral regions and converting each region with a cell (junction) whose band gap is tuned for good absorption in that region. Typical energy gaps of materials are between 0.7-2 eV [2] with efficiency >30% from a combination of III-V semiconductors, e.g. GaP (2.25 eV), InP (1.27 eV), GaAs (1.42 eV), InAs (0.36 eV) [3]. Series of materials with closely lattice parameters are also crucial to prevent a lattice mismatch [2] accommodated by nucleation and propagation of dislocations - leading to the non-radiative recombination which is an undesired process that limits efficiency of a device. The finely band gap tuning via solid-solution of III-V semiconductors achieves appropriate band gaps with closely lattice-matched yielding high efficiency, i.e., 41.6% in Ga_{0.5}In_{0.5}P (1.85 eV)/ Ga_{0.99}In _{0.01}As (1.39 eV)/ Ge (0.67 eV) cell from Spectrolab (USA) [4]. The lattice matching is easier attained in a cationic solidsolution since the change in cation's size is smaller than that of anion. In Chapter 3, we demonstrate a potential candidate for a new class of solar absorber material on basis of earth-abundant Cu₃PS_{4-x}Se_x system, which represents band gap in range of 1.35-2.36 eV previously discussed in Chapter 3. Thus, we chose to expand our studies to lower periods of group 15 elements, e.g. Cu₃AsS₄, Cu₃SbS₄.

Cu₃PS₄ and Cu₃AsS₄ are orthorhombic cell, with space group $Pmn2_1$ (Fig. 4.1a). Their structures are modified ZnS-wurtzite structure type (see details in Chapter 3), whereas famatinite Cu₃SbS₄ [5] crystallizes in tetragonal cell, with space group *I-42m* (Fig. 4.1b) adopting a ZnS-sphalerite structure type, where Cu⁺ and Sb⁵⁺ are in tetrahedral sites, and S²⁻ arrays are approximate cubic closed packing. A formation of cationic solid solution in these materials was reported in Cu₃AsS₄-Cu₃SbS₄ system by Pfitzner and coworker [6]. They studied on crystallographic details of structural conversion between orthorhombic-tetragonal, and found that $Cu_3As_xSb_{1-x}S_4$ became orthorhombic unit cell when x > 0.8. We measured band gap of Cu_3SbS_4 powder from diffuse reflectance technique and found the absorption onset to be ~0.9 eV. $Cu_3(P, As, Sb)S_4$ shows good capability to tune band gap in the whole range of 1-1.8 eV for multijunction solar cell application. This Chapter demonstrates optical and electrical properties of $Cu_3P_xAs_{1-x}S_4$ and $Cu_3P_xSb_{1-x}S_4$ systems.



Fig. 4.1 a) Cu₃(P, As)S₄ structure b) Cu₃SbS₄ structure.

4.2 Experimental

4.2.1 Sample preparation and phase identification

Appropriate amount of high purity elemental powders of Cu (99.999%, Alfa Aesar), P (99.9999+%, Alfa Aesar), As (99.99%, AlfaAesar), Sb (99.9999%, Alfa Aesar), and S (99.999%, Alfa Aesar) were ground thoroughly, and sealed in evacuated fused silica tubes. $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$) were obtained via heating evacuated sealed silica tubes for 24 h at 500 °C with another regrinding, and reheating for 24 h at the same reaction temperature. Cu_3SbS_4 was obtained in a similar way at reaction temperature 450-480 °C with additional 1-2 regrinding, and reheating at the same reaction temperature. $Cu_3P_xSb_{1-x}S_4$ (0 < x < 1) were attempted between 450-600 °C, but did not yield solid solution phases. Powder X-ray diffraction (XRD) data were collected with a Rigaku Ultima IV diffractometer, utilizing Cu K α radiation. Lattice parameters of powder samples were obtained by the use of PDXL software [7]. $Cu_3P_xAs_{1-x}S_4$ pressed powder pellets of 0.5" diameter were used to characterize optical and electrical properties. The samples were cold pressed at 3-4 tons, and then sintered at synthesis temperature for 24 h in evacuated sealed tubes. Final pellet densities were approximately 75-82% of theoretical values.

4.2.2 Optical and electrical measurement

Optical band gaps were estimated by diffuse reflectance measurements utilizing an Ocean Optics HR4000 UV-VIS spectrometer with a DH-2000-BAL balanced deuterium/tungsten halogen source. MgO powder (99.95%, Cerac) was used as a reference. Room temperature resistivity and Hall mobility were measured in the van der Pauw geometry using a LakeShore 7504. Majority-carrier type was determined from Seebeck measurements on an custom system applying a ~3 °C temperature gradient on the samples.

4.3 Results and Discussion

4.3.1 Phase characterization

The powder XRD patterns of $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$) are shown in Fig. 4.2. The experimental Cu_3PS_4 and Cu_3AsS_4 patterns are similar to their calculated patterns [5, 6]. The solid solutions have peak positions between those of Cu_3PS_4 and Cu_3AsS_4 with similar relative intensities. All peaks shifts toward larger 20 because of contractions of the lattice parameters (Fig. 4.3) and unit cell volume (Fig. 4.4) from x = 0 (Cu_3AsS_4) to x = 4 (Cu_3PS_4) associated by P substitution to As sites. Since the Shannon's effective ionic radii [8] of 4-fold coordination of P^{5+} and As^{5+} (Table 4.1) are not significant difference, the formation of solid-solution of $Cu_3P_xAs_{1-x}$ are observed. Similar explanation can be applied to previously reported $Cu_3As_xSb_{1-x}S_4$ [6]. However, $Cu_3P_xSb_{1-x}$ solid-solution did not form

at the reaction temperature between 450-600 $^{\circ}$ C, and found a phase separation of Cu₃PS₄ and Cu₃SbS₄ (Fig. 4.5). Considering a difference in size of P⁵⁺ and Sb⁵⁺ are too large, hence P⁵⁺ is not well stabilized in tetragonal unit cell of Cu₃SbS₄ structure. Similar situation could be presumed to a non-stabilized Sb⁵⁺ in orthorhombic Cu₃PS₄ structure.



Fig. 4.2 X-ray diffraction patterns of $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$).



Fig. 4.3 Lattice parameters plot of $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$).



Fig. 4.4 Unit cell volume of $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$).

Cation	CN = 4	CN = 6
Cu ⁺	0.60	0.70
P ⁵⁺	0.17	0.38
As ⁵⁺	0.335	0.46
Sb ⁵⁺	n/a	0.60

Table 4.1 Shannon's effective ionic radii (Å) [8] for coordination number (CN) = 4 and 6 of Cu⁺, P⁵⁺, As⁵⁺ and Sb⁵⁺.



Figure 4.5 X-ray diffraction patterns of $Cu_3P_xSb_{1-x} S_4$ ($0 \le x \le 1$). Phase separation of Cu_3PS_4 and Cu_3SbS_4 were shown in all 0 < x < 1. Calculated XRD patterns of Cu_3PS_4 and Cu_3SbS_4 were simulated from ICSD #412240, #412239, respectively.

4.3.2 Optical characterization

Optical band gaps of $Cu_3P_xAs_{1-x}Se_x$ series, estimated from E vs k/s plot from diffuse reflectance measurements, were illustrated in Fig. 4.6. Experimental band gaps increase from 1.3 eV (x = 0, Cu_3AsS_4) to 2.36 eV (x = 4, Cu_3PS_4). The band gap does not change linearly - slowly increasing in x = 0 to 0.8, and dramatically change between x = 0.8 to 1. We hypothesized on basis of a band structure of Cu_3PS_4 (detail in Chapter 5), which P atoms contribute much of s states (s band) at the conduction band minimum (CBM). The lower energy level of s and p states of P, i.e., 3s and 3p orbitals, (compared to 4s and 4p orbitals of As), could push down valence band maximum (VBM), and raises the empty s-bands energy level at the CBM, resulting in a widen band gap energy. The more P composition (increase in x), the more density of states of P contribution, and the higher band gap obtain. Also, a nature of band gap is probably switched between direct gap in Cu_3AsS_4 and indirect gap of Cu_3PS_4 [9].

Intermediate solid solutions of $Cu_3P_xAs1_xS_x$ with x = 0, 0.2, and 0.8 exhibited an onset of absorption near 1.3, 1.4, and 1.7 eV, respectively. These band gaps showed good ranges for middle (1.3-1.4 eV) and top (1.7 eV) of multijunction solar cell in a single material set with closely lattice parameters (Fig. 4.3). For the bottom cell (~1 eV), we

expect the Cu_3SbS_4 (Eg ~0.9 eV) is a good abosrober candidate. Solid solution between Cu_3AsS_4 - Cu_3SbS_4 will be applicable for tuning band gap in range of 0.9-1.3 eV.



Fig. 4.6 Band gap of $Cu_3P_xAs_{1-x} S_4$ ($0 \le x \le 1$).

Table 4.2 Resistivity and Seebeck coefficient of $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$).

	x = 0	x = 0.2	x = 0.4	x = 0.6	x = 0.8	x = 1
Resistivity	55	42	90	98	120	933
(Ω cm)						
Seebeck	+530	+660	+668	+753	+848	+674
(μV Κ⁻¹)						



Fig. 4.7 Carrier concentration (close square) and hole mobility (open square) of $Cu_3P_xAs_{1-x}$ S_4 (0 ≤ x ≤ 0.8).

4.3.3. Electrical characterization

Resistivity and Seebeck coefficients measured on pressed pellets are summarized in Table 4.2. All samples demonstrate high positive Seebeck coefficients (> 100 μ V K⁻¹) indicating characteristic of *p*-type semiconductor. Hole carrier concentrations derived from Hall coefficients (Fig. 4.7) are in range of 10¹⁶ cm⁻³, in good agreement with measured large, positive Seebeck coefficients. An increasing in resistivity from Cu₃AsS₄ (x = 0) to Cu₃PS₄ (x = 4) is observed, and accompanied by decrease in hole mobility (Fig. 4.7) with the rise of P content. However, mobility and carrier concentration could not be measured from Cu₃PS₄ pellets.

High mobilities in $Cu_3P_xAs_{1-x}S_4$ pressed pellets $(1 \sim 11 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1})$ are impressive as we experienced similar phenomena from $Cu_3PS_{4-x}Se_x$ system previously discuused in Chapter 3, i.e., hole mobility of Cu_3PSe_4 was measured $\sim 13 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$. High covalency of As-S bonding encourages delocalization of charged carriers and high hole mobility. Typically, Hall mobility is hard to measure in pressed pellets due to porosity of samples, and grain boundary inhibited transportation associated with a polycrystalline microstructure [10]. Similarly to Cu₃PS_{4-x}Se_x system, the surfaces of Cu₃PS_{4-x}Se_x could be rather benign with respect to scattering charged carriers - facilitating delocalization of the charged carriers resulting in high carrier mobility.

Furthermore, the covalent nature of this system represented relatively low carrier concentration compared to those of typically Cu-based chalcogenides (typically > 10¹⁸ cm⁻ ³) [11-13]. Enhanced covalency arose from P-S and As-S bonding, higher Cu vacancy formation energies would be expected leading to reduced hole concentrations and also higher mobilities because of reduced ionized impurity scattering.

4.4 Summary

We report optical and electrical properties of $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$). Band gap of this system demonstrates in range of 1.3-2.36 eV. Seebeck measurements show majority holes carriers with electrical semi-conducting behavior. Higher As:P ratio enhances hole mobility up to ~11 cm² V⁻¹ s⁻¹, and carrier concentration in range of 10¹⁶ cm⁻³. Wide range of band gap in $Cu_3P_xAs_{1-x}S_4$ is potentially useful for multijunction PV application. Eventhough $Cu_3P_xSb_{1-x}S_4$ could not be achieved solid-solution formation, there are still potential systems in $Cu_3PS_{4-x}Se_x$ and $Cu_3P_xAs_{1-x}S_4$ available, such as $Cu_3As_xSb_{1-x}S_4$, $Cu_3AsS_{4-x}Se_x$, to expand and develop novel class materials of solar absorbers for both single and multijunction PV.

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Synthesis, crystal structure, and electronic structure of CuZnPS₄

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5.1 Introduction

Research on photovoltaic (PV) and photocatalytic materials has been carried out for a long time and gained much popularity due to the utilization of solar energy – a renewable and sustainable energy resource [1]. An earth-abundance, non-toxic and lowcost inorganic semiconductor is attractive for applications in solar energy conversion and solar fuel generation via H_2O and H_2S splitting in photoelectrochemical cells requiring band gap energies in the 1.1-2.4 eV [2]. Current chalcogenide candidates such as binary CdS, ternary CuInSe₂, quaternary Cu(In, Ga)S₂ do not meet all of the above criteria due to toxicity of Cd and the rarity of In. To our best knowledge, very few Cu-Zn chalcogenides have been synthesized. The only well-known ones are stannite and kesterite phases of Cu₂ZnSn(S, Se)₄, a promising solar absorber in PV cell research [3].

All of above mentioned compounds have modified diamond-liked tetrahedral structure; where only 50% of tetrahedral sites are filled by cations. In binary system, well known ZnS is exist in both cubic sphalerite phase, where S arrays are cubic closed packing (ccp), and hexagonal wurtzite phase if hexagonal closed packing (hcp) of S. In ternary system, widespread studied tetragonal chalcopyrite group of compounds e.g. CuFeS₂, CuGaSe₂, CuInSe₂ is modified structure from sphalerite-ZnS, whereas an orthorhombic enargite group [4-6] e.g. Cu₃PS₄, Cu₃AsS₄ is modified wurtzite-ZnS structure. When tetrahedral sites are filled less than 50%, a defect tetrahedral structure is created, and first discovered in the ternary system described as defect chalcopyrite because of close relation to chalcopyrite structure with only 3/8 of tetrahedral sites filled by cations i.e. A_2BQ_4 (A = AI, Ga, In; B = Zn, Cd, Hg; Q = S, Se, Te) [7-10]. Defect chalcopyrites show good promising for optoelectronic applications because of characteristic high non-linear susceptibility and photosensitivity [9]. Defect chalcopyriteliked structure is also found in halides e.g. Cu₂Hgl₄ [11]. Nevertheless, there are still very few compounds crystallized in this type of structure especially in quaternary system; advantageous over ternary system due to better providing flexibility for tuning composition and property. To explore new Cu-based chalcogenide, we started with ternary orthorhombic Cu₃PS₄, a p-type semiconductor with an indirect band gap of 2.38 eV [5], and created a defect structure by replacing Cu⁺ with Zn²⁺ leading to a formation of new earth abundant quaternary compound, CuZnPS₄. In this work, we discussed crystal structure refinement, optical and electronic structure of CuZnPS₄ in comparison to Cu₃PS₄ with respect of structural relation to their properties.

5.2 Experimental

5.2.1 Powder sample preparation

Powder samples of CuZnPS₄ were synthesized by solid state reaction of elemental mixtures of Cu (Alfa Aesar, 99.999%), Zn (Cerac, 99.9%), P (Materion, 99.999+%) and S (Cerac, 99.999%). Stoichiometic quantities of the elements were ground, sealed in evacuated fused silica tubes, and then heated at 540 °C for 24 h; grinding and heating were repeated two or three times. Samples of Cu₃PS₄ were prepared in the similar, except heating was done at 550 °C. Solid solution samples CuZnPS_{4-x}Se_x (0 $\leq x \leq 4$) with Se (Alfa Aesar, 99.999%) were also heated at temperatures up to 540 °C. 12.7-mm pellets for electrical measurements were pressed at 4 tons (room temperature) and then sintered in evacuated, sealed silica tubes at 580 °C for 24 h. The final densities of the CuZnPS₄ and Cu₃PS₄ pellets were approximately 85% and 70%, respectively, of theoretical values.

5.2.2 Single crystal growth and compositional analysis

CuZnPS₄ single crystals were grown in sealed, evacuated silica tubes by chemical vapor transport using NH₄Br (Alfa Aesar, ACS, 99.999%) as the transport agent (3 mg/cm³ of tube volume). A temperature gradient was established across a 3-zone Applied Test Systems tube furnace by setting the three temperatures to 550 °C (T1), 650 °C (T2) and 750 °C (T3). The system was then cooled at a rate of 4 °C/h to the temperatures 300°C (T1), 400 °C (T2), 500 °C at which point the power to the furnace was turned off. Pale yellow crystals were collected from the cool end of the tube. The elemental analysis was

acquired on an Inductively coupled plasma optical emission spectrometry (ICP-OES) on Jobin Yvon JY2000.

5.2.3 Structural Characterization

X-ray diffraction data for powder samples were collected with a Rigaku Ultima IV Diffractometer, utilizing Cu K α radiation. Lattice parameters were refined and obtained by the use of PDXL software [12]. Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer at 173(2) K with Mo K α radiation. The space group was determined on the basis of the observed Laue symmetry and the systematic absences. The structure was solved using direct methods and Fourier techniques and then refined on F² with full matrix least-squares methods. An absorption correction was applied by using the program SADABS [13]. The crystal was found to be a racemic twin; the Flack parameter is 0.74(3). All atoms were refined with anisotropic thermal parameters. All software and sources of scattering factors for the calculations are contained within the SHELXTL 6.10 package [14].

5.2.4. Optical and Electrical Characterization

Optical band gaps were determined by diffuse reflectance with a spectrometer comprising an Ocean Optics HR4000 UV-VIS detector and a DH-2000-BAL balanced deuterium/tungsten halogen source. The white reference for diffuse reflectance was MgO powder (Cerac, 99.95%). Reflectance spectra were converted to absorbance according to the Kubelka-Munk theory [15, 16] and Equation (5.1),

$$F(R) = (1 - R)^2 / 2R = k/s$$
 (5.1)

where R = corrected reflectivity from $R_{sample}/R_{standard}$, k = absorption coefficient and s = scattering coefficient. An approximate optical band gap is extracted from a k/s *vs.* E (eV) plot.

A test for second-harmonic generation was made by using a pulsed Nd:YAG laser with NLO α -SiO₂ as the reference. The methods and setup have been described

elsewhere [17, 18]. The measurement was performed by Thanh Thao Tran from Halasyamani's research group, Department of Chemistry, University of Houston.

Room temperature resistivity data were obtained from a pressed pellet by using the van der Pauw geometry with indium as metal contacts; data were collected with a LakeShore 7504 Hall Measurement System. Majority carrier type was determined from Seebeck measurements on a custom designed system.

5.2.5. Electronic structure calculation

Electronic and optical properties of $CuZnPS_4$ and Cu_3PS_4 were calculated using the Wien2k package [19]. The relaxed unit-cell parameters of $CuZnPS_4$ and Cu_3PS_4 were expanded on a 14 x 14 x 14 and 13 x 14 x 15 k-mesh, respectively. The GGA+U with the self-interaction correction method was employed to the Cu 3d orbitals by using U = 6.4 eV.



Fig. 5.1 Crystal structure of (a) Cu₃PS₄ (Pmn2₁) and (b) CuZnPS₄ (I-4).

5.3 Results and Discussion

First, let us consider the Cu_3PS_4 structure (Fig. 5.1a) which crystallizes in orthorhombic space group Pmn2₁ (no. 31). This 3-dimensional framework structure

consists of corner sharing of tetrahedral [CuS₄] and [PS₄] units, which coordination numbers (CN) of Cu, P and S are 4. The S arrays are hcp with half-filled tetrahedral sites by cations, thus Cu₃PS₄ can be categorized as a modified wurtzite-ZnS structure. The bond lengths of Cu-S and P-S are about ~2.32 Å and ~2.07 Å, respectively [4]. The S-Cu(1)-S and S-P-S angles are close to ideal tetrahedral angle, while the S-Cu(2)-S angles are deviated up to 5 degrees causing distortion around Cu(2) centers. Due to a significant difference in cation sizes between Cu⁺ and P⁵⁺, the size of [CuS₄] and [PS₄] polyhedra will be also large difference leading to distortion in the structure, where the hcp could compensate the distortion better than ccp [4].

In CuZnPS₄ structure (Fig. 5.1b), it crystallizes in the space group I-4 (no. 82) of tetragonal system consisting of corner sharing of [CuS₄], [ZnS₄] and [PS₄] similar to Cu₃PS₄ However, introducing Zn²⁺ into the structure while maintaining charge balancing results in only 3/8 of tetrahedral sites occupied by cations. The S packing is approximate ccp with S coordinated to Cu, Zn and P (CN of S = 3). The crystal data and structure refinement of CuZnPS₄ is showed in Table 5.1-5.4. The bond lengths of Cu-S (~2.33 Å) and P-S (~2.05 Å) in CuZnPS₄ are about the same as those in Cu₃PS₄. On the other hand, the S-Cu-S and S-P-S angles in CuZnPS₄ are more deviation up to 5 and 9 degrees, respectively. The large bond angle deviation might be from the presence of nonbonding lone pair of electrons from three-fold coordination of S which needs large space to reduce electrostatic repulsion at the tetrahedral centers. Although hcp of anions and orthorhombic unit cell in CuZnPS₄ could be expected due to the large distortion from extremely distorted tetrahedral centers, ccp type and tetragonal unit cell maybe allows more stabilized structure for three-fold coordination of S. To date, it is still an open discussion why certain compounds prefer hcp or ccp of anions.

Compositional analysis of the crystals were determined by ICP-OES and obtained averaged stoichiometry of $Cu_{0.95\pm0.04}Zn_{1.04\pm0.03}P_{1.05\pm0.07}S_{4.12\pm0.16}$; quite close to theoretical formula of $CuZnPS_4$.

Empirical formula	CuZnPS ₄
Formula weight	288.12
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	I-4
Unit cell dimensions	a = b = 5.4939(7), c = 9.233(2) Å
	$\alpha = \beta = \gamma = 90^{\circ}$
Volume	278.69(9) Å ³
Z	2
Density (calculated)	3.434 g/cm ³
Absorption coefficient	9.744 mm ⁻¹
F(000)	276
Crystal size	0.06 x 0.05 x 0.02 mm ³
Theta range for data collection	4.32 to 27.86°
Index ranges	-7 ≤ h ≤ 7, -7 ≤ k ≤ 7, -12 ≤ l ≤11
Reflections collected	1616
Independent reflections	328 [R(int) = 0.0183]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8290 and 0.5925
Data / restraints / parameters	328 / 0 / 18
Goodness-of-fit on F ²	1.192
Final R indices [I>2sigma(I)]	R1 = 0.0160, wR2 = 0.0413
R indices (all data)	R1 = 0.0160, wR2 = 0.0413
Absolute structure parameter	0.74(3)
Extinction coefficient	0.041(2)
^a R1= Σ($ F_0 $ - $ F_c $) / Σ $ F_0 $ ^b	wR2 = $[\Sigma {w(F_0^2 - F_c^2)}^2 / \Sigma w F_0^2]^{1/2}$

Table 5.1 Crystal data and structure refinement for CuZnPS₄ at 173(2) K.

Atom	Wyckoff	x	У	Z	U (eq)	Occupancy
	sites					
Cu	2b	0	0	0.5	0.009(1)	1
Zn	2a	0	0	0	0.011(1)	1
Р	2c	0	0.5	0.25	0.007(1)	1
S	8g	0.7737(2)	0.2722(2)	0.1370(1)	0.008(1)	1

Table 5.2 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for CuZnPS₄. U(eq) is defined as one third of the trace of the orthogonalized U_{ii} tensor.

Table 5.3 Anisotropic displacement parameters (Å²) for CuZnPS₄. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2h k a^* b^* U^{12}]$

Atom	U^{11}	U ²²	U^{33}	U^{23}	U^{13}	U^{12}
Cu	0.009(1)	0.009(1)	0.009(1)	0	0	0
Zn	0.011(1)	0.011(1)	0.010(1)	0	0	0
Р	0.007(1)	0.007(1)	0.005(1)	0	0	0
S	0.007(1)	0.008(1)	0.009(1)	-0.001(1)	-0.002(1)	0.000(1)

Symmetry transformations used to generate equivalent atoms:

#1 y-1/2,-x+1/2,-z+1/2 #2 x-1/2,y-1/2,z+1/2 #3 -y+1/2,x-1/2,-z+1/2

#4 -x+1/2,-y+1/2,z+1/2 #5 -y,x-1,-z #6 x-1,y,z #7 y,-x+1,-z #8 -x+1,-y,z

#9 -x+1,-y+1,z #10 y-1/2,-x+3/2,-z+1/2 #11 x+1,y,z #12 x+1/2,y+1/2,z-1/2

Table 5.4 Selected bond lengths (Å) and bond angles (°) for CuZnPS₄.

 Cu-S	2.3294(14)	S#5-Zn-S#7	113.94(5)	
Zn-S	2.3198(14)	S#6-P-S#3	105.03(2)	
P-S	2.0497(7)	S#6-P-S#9	118.77(4)	
S#1-Cu-S#2	107.14(3)	P-S-Zn	110.25(5)	
S#1-Cu-S#3	114.24(5)	P-S-Cu	109.88(6)	
S#5-Zn-S#6	107.29(3)	Zn-S-Cu	113.35(3)	

Our crystal structure refinement is on basis of ordered structure, where Cu(I) and Zn(II) occupation are in different sites, in similar way as done in LiZnPS₄ [20] and AgZnPS₄ [21]. However, typical XRD technique cannot distinguish the difference between Cu(I) and Zn (II) because they are isoelectronic in principle resulting in very close scattering factors. Since, Shannon effective ionic radii in 4-fold coordination of Cu(I) and Zn(II) are very close [22], bond distance in CuZnPS₄ (Table 5.4) between Cu-S and Zn-S become ~2.33 Å and for ~2.32 Å, respectively. By similar in size and isoelctronic of Cu(I) and Zn(II) infer a possibility of disordering of cations in this structure; Zn (II) and Cu (I) occupy the same site in a certain ratio as found in Cu₂ZnSnS₄ structure (I-42m, ICSD #171983) [23]. However, Cu₂ZnSnSe₄ (I-42m, ISCD#95117) [24] is refined as an ordered structure, different occupied sites of Cu(I) and Zn(II), as similar to Cu₂CdSnSe₄ and Cu₂HgSnSe₄ [24].

The further studies to obtain more structural details on CuZnPS₄ are needed to be able to determine actual Cu/Zn site occupation i.e. specific refinement on Cu and Zn sites bases upon Cu: Zn ratio result obtained by ICP-OES.

CuZnPS₄ powders were successfully synthesized and obtained XRD pattern as shown in Fig. 5.2. The formation of S-Se solid solution in CuZnPS_{4-x}Se_x were found in range of $0 \le x \le 1.5$, while the higher Se:S ratio at x > 1.5 leaded to phase separation of Cu₃P(S,Se)₄ and Zn(S,Se) shown in Fig. 5.3. The lattice parameter (Fig. 5.4) and unit cell volume (Fig. 5.5) of CuZnPS_{4-x}Se_x show unit cell expansion when increasing of x up to x = 1.5 as the solubility limitation of Se substitution into S sites.



Fig. 5.2 Powder XRD pattern of CuZnPS₄.



Fig. 5.3 Powder XRD patterns of $CuZnPS_{4-x}Se_x$ ($0 \le x \le 4$).



Fig. 5.4 Lattice a and c parameters of $CuZnPS_{4-x}Se_x$ ($0 \le x \le 1.5$).



Fig. 5.5 Unit cell volume of $CuZnPS_{4-x}Se_x$ ($0 \le x \le 2$).



Fig. 5.6 Band structures and projected DOS plots of $CuZnPS_4$ (Top) and Cu_3PS_4 (Bottom). E_F position is at E = 0.

The electronic structures of CuZnPS₄ and Cu₃PS₄ have been calculated on the basis of the GGA+U approach. Band structures and projected densities of states (DOS) are given in Fig. 5.6. For Cu₃PS₄, the valence band maximum (VBM) is located at the Γ point, and it is characterized primarily by Cu 3d and S 3p orbital characters. If we consider crystal filed splitting of tetrahedral d¹⁰ Cu(I), all 3d orbitals are full filled, thus it is sensible to observe a lot of contribution from Cu 3d at VBM. The conduction band minimum (CBM)

is located at the Z point, and it is characterized by majority contributions from P 3s and S 3p orbitals; P clearly plays a major role with respect to the character of the CBM. A small amount of Cu 4s character is located slightly higher in the conduction band – corresponding to empty 4s orbital of d^{10} Cu(I). With the VBM at Γ and the CBM at Z, the material is predicted to have an indirect gap.

For CuZnPS₄, the orbital contributions to the VBM and CBM are similar to those of Cu_3PS_4 . The S 3p density of states, however, is much higher, reflecting the three-fold coordination of S and the presence of a nonbonding lone pair of electrons. Again, the character of the CBM is mainly P 3s and S 3p. Contributions from Cu and Zn 4s bands are minimal, as they are located approximately 1 eV above the CBM. The VBM is located at the X-point and the CBM is at the Z point, indicating the material should have an indirect gap.



Fig 5.7 Optical absorption of $CuZnPS_4$ and Cu_3PS_4 . (a) Diffuse reflectance (b) Calculated absorption spectra.

The calculated band gap for $CuZnPS_4$, 2.33 eV, compares favorably to the observed gap of 2.4 eV, see Fig. 5.7a. For Cu_3PS_4 , however, the calculated gap, 1.67 eV, and observed gap, 2.3 eV, differ significantly. The differences in calculated energies between the direct and indirect gaps for $CuZnPS_4$ and Cu_3PS_4 are 0.07 and 0.05 eV, respectively. As shown in Fig. 5.7b, the sharp onsets in absorption occur at energies

associated with the direct transitions. High absorption ($\alpha > 10^5$ cm⁻¹) is predicted for each compound at Eg + ~1 eV.



Figure 5.8 SHG intensity vs particle size data for CuZnPS₄. The curve was drawn to guide the eye, and was not a fit to the data.

Because CuZnPS₄ crystallizes in a noncentrosymmetric space group, it is expected to have a nonzero nonlinear optical susceptibility. Indeed, because the M-S vectors are all approximately aligned, the susceptibility coefficient is expected to have a reasonable magnitude. A second harmonic generation (SHG) measurement from a powder with a 1064-nm laser fundamental produced a signal (Fig. 5.8) ~240 x α -SiO₂ (~6 x KH₂PO₄ (KDP)) with a non-phase matching – SHG signal is not proportional to particle size of material. This signal corresponds to d_{eff} ~ 11 pm/V. For comparison, the nonlinear coefficients for ZnS crystals are reported as d₃₆ (sphalerite) ~50 pm/V, and d₃₃ (wurtzite) ~ 28 pm/V [25]. Although, Cu₃PS₄ also crystallizes in a non-centrosymmetric space group, frequency doubling from 1064 nm excitation is not apparently observed in its powder sample.

Resistivity data from pressed pellets of CuZnPS₄ could not be obtained, as the material is highly insulation. Measurements on pressed pellets of Cu₃PS₄ gave resistivity values in the range of 500-600 Ω cm. with Seebeck coefficient of +650 to +670 μ V K⁻¹ establishing the hole carrier type, without external doping. The insulating behavior in CuZnPS₄ can be explained by lacking of conduction pathway (via Cu vacancies) through Cu-S-Cu connectivity in the structure. There are only Cu-S-Zn, Cu-S-P and Zn-S-P linkages in case of ordered structure resulting in minimal band development with respect to Cu-S-Cu dispersion (F-X direction) as observed in calculated band structure of CuZnPS₄ in Fig. 5.6 (Top). Electron conduction is also diminished by the highly localized P 3s bands near the CBM due to absence of linkage between [PS₄] tetrahedra. In case of disordering of Cu and Zn occupation, the conduction pathway is still disrupted. Zn(II) substituted in Cu(I) site will act as a hole killer i.e. electron donor increasing electron concentration [26, 27]. At the same time, Cu(I) in Zn(II) site will be an electron killer, so that the case of Cu-Zn disordering dose not dramatically change electrical conduction related to cation ordered structure model as previously explained. Also, there is no carrier generation or transporting via Zn-S-Zn linkages. On the other hand, semiconducting behavior in Cu₃PS₄ is observed since this structure contains good Cu-S-Cu linkages as a conduction pathway in all 3 directions; agreeing with high dispersion at VBM in calculated band structure of Cu₃PS₄ as shown in Fig. 5.6 (Bottom).

5.4 Summary

We discover CuZnPS₄ as a new quaternary Cu-based chalcogenide on basis of Zn substitution into orthorhombic Cu₃PS₄; a modified wurtzite-ZnS structure. Tetragonal CuZnPS₄ is a defect chalcopyrite which is a modified sphalerite-ZnS structure with less than 50% of cation occupation in tetrahedral sites. Single crystal structure refinement on CuZnPS₄ is done based upon ordered structure, where Cu(I) and Zn(II) occupation are in different sites. Optical property in CuZnPS₄ (2.4 eV) and Cu₃PS₄ (2.3 eV) is quite similar in aspect of band gap energy and absorption property ($\alpha > 10^5$ cm-1 within Eg + ~1 eV), but

only CuZnPS₄ shows strong SHG response (~240 x α -SiO₂). Electrical property of two materials is very different related to their structures. Cu₃PS4 shows semi-conducting behavior (p-type) because Cu-S-Cu connectivity as a conduction pathway are well established all 3 directions in the structure, whereas CuZnPS₄ is an insulator since the lack of Cu-S-Cu linkages caused from large isolation of Cu by Zn substitution. Although, Cu-Zn disordered occupation might occur, this situation does not improve conduction pathway in the structure.

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Chapter 6

New green Up-conversion phosphor YZrF₇:Ln³⁺

(Ln = Yb, Er, Yb/Er)

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6.1 Introduction

The up-conversion process [1-2] which converts near infrared radiation (NIR) into visible light has grown interests in the fields of the lighting and display technology and solar energy conversion. Under NIR excitation, introducing rare-earth lanthanide ions e.g. Yb³⁺/Er³⁺ or Yb³⁺/Tm³⁺ in a proper host can show green and blue emissions, respectively. There are some compounds reported to be up-conversion hosts such as YF_3 [3], NaYF₄ [4], NaGdF₄ [5], KYF₄ [6], Y₂O₂S [7]. Among of the candidate hosts, the hexagonal structure NaYF₄ is known to show the highest luminescence efficiency [4]. Poulain and coworkers [8] solved the crystal structure of SmZrF7, and provided lattice parameters of YZrF7 from the powder XRD result. However, structural establishment of single crystal of $YZrF_7$ has not been provided. Also, there is no study of this compound as an upconversion host phosphor. The YZrF₇ contains heavy elements of Y and Zr, which could induce the low phonon energy promising high up-conversion efficiency by suppressing the non-radiative energy loss. In this work, the single crystal of YZrF₇ was grown and reported crystal structure. The polycrystalline samples were prepared, and investigated luminescent characteristics when doping with Eu³⁺, Tb³⁺, Er³⁺ and Yb³⁺/Er³⁺. The YZrF₇: Yb³⁺, Er³⁺ was also compared up-conversion luminescence to NaYF₄: Yb³⁺, Er³⁺.

6.2 Experimental Section

6.2.1 Sample preparation

YZrF₇ doped with Ln³⁺ (Ln = Er, Eu, Tb, Yb/Er) were synthesized by mixing the stoichiometric of quantity of YF₃ (Alfa Aesar, 99.9%), ZrF₄ (Sigma-Aldrich, 99.9%), YbF₃ (Alfa Aesar, 99.9%), ErF₃ (Alfa Aesar, 99.99%), Eu₂O₃ (Stanford Materials Corporation, 99.99%) and TbF₃ (Alfa Aesar, 99.9%) with additional NH₄F (J.T.Baker, reagent grade). The other Y sources used in this work were $Y_2(C_2O_4)_3 \cdot 9H_2O$ (Alfa Aesar, 99.9%) and Y_2O_3 (Standford Materials Corporation, 99.99%). All powders were grounded and put in a carbon crucible, which was encapped by an alumina crucible. Both crucibles were put in a

bigger alumina crucible filled with carbon power for creating inert atmosphere. The crucibles were heated at 650° C for 1.5 h, then grinded and added extra NH₄F before heated to 750° C for 1.5 h, and cooled down naturally to room temperature. Hexagonal NaYF₄:18%Yb³⁺, 2%Er³⁺ samples were prepared by similar method as used for YZrF₇. The firing temperature was 630 °C [9] for 2 h. The samples were characterized by XRD and obtained the pattern agreeing with ICSD# 51921 and [4].

6.2.2 Characterizations

Powder X-ray diffraction (XRD) was collected by a Rigaku MiniFlex II X-ray Diffractometer utilizing Cu K α 1 radiation (λ = 1.54059 Å). The X-Ray diffraction data from a YZrF7 single crystal was collected on a Bruker Smart Apex diffractometer at 173(2) K using Mo K α radiation (λ = 0.71070 Å). The structure was solved using direct methods, and refined with full-matrix least-squares methods based on F². All calculations were performed using the SHELXTL (v. 6.10) package [10]. SEM images were obtained by FEI Quanta 600 FEG SEM. The emission spectra were obtained by exciting the sample with an Oriel 66011 UV lamp and a 100 mW 980 nm NIR World Star Tech, UH5-100G-980 laser diode. The visible emissions from the samples were dispersed with an Acton Spectrapro-150 spectrometer, and were detected with a Hamamatsu R636-10 photo multiplier tube (PMT) and the electric signals were delivered to computer. The average brightness of samples was measured by the same PMT tube without dispersing the emission output into monochromator under the fixed intensity of NIR laser. The emission outputs were collected 30 minutes. All emission spectra and brightness were measured at room temperature. Diffuse absorption spectra were collected by diffuse reflectance spectroscopy using a Si photodiode mounted on an Oriel 70491 integrating sphere. The sample was placed in a ceramic holder beneath the sphere, and light from an Oriel-150 W Xe lamp was directed through a Oriel 77250 double-monochromator and a series of mirrors into the top of the sphere. The measurements were carried out at room temperature and using MgO powder (Cerac, 99.95%) as a standard reference.

6.3 Results and Discussion

6.3.1 Crystal structure

Some views of crystal structure of YZrF₇ drawing are given in Fig. 6.1. YZrF₇ crystallizes in monoclinic unit cell system with space group P2₁/m (No. 11) consisting of 8-coordinated [YF₈] units corned sharing with 6-coordinated [ZrF₆] units. The coordination environment of Y³⁺ is similar to orthorhombic YF₃ [11]. YZrF₇ is isostructural to SmZrF₇ (P2₁) [8], but YZrF₇ was solved and refined in space group P2₁/m, which showed better refinement data than P2₁. One of F atoms (a μ_2 -bridge connecting Y atoms) is disordered over two positions related by a mirror plane. Hence, two zig-zag -Y-F-Y-F- chains with different positions of the bridging F atoms are existed in the crystal, but with the same occupations as demonstrated in Fig. 6.2. The Y-F bond lengths are in ranges of 2.150(6) – 2.341(4) Å, while, those of Zr-F are only 1.980(4) - 1.998(4) Å. The full crystallographic data of YZrF₇ including atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths, and bond angles are represented in Tables 6.1-6.4.

6.3.2 Phase characterization and morphology

The experimental XRD patterns of YZrF₇ seen in Fig. 6.3 show single phase, and have good agreement with a calculated pattern based on single crystal structure refinement. The slightly peak shifts to larger 20 found in doped samples with M^{3+} substitution to Y^{3+} (M = Eu, Tb, Er, Yb), because of unit cell contraction. The maximum peak intensity in undoped sample is centered at ~21.7° corresponding to the (110) plane, while, the shifting is ~0.1° in co-doped 25%Yb and 2%Er sample. The difference in Y source affects overall peak intensity, but relative intensity in the same samples do not change. Hence, crystallinity of samples in different Y sources is in order of Y₂O₃> YF₃ > Y₂(C₂O₄)·9H₂O. SEM images (Fig. 6.4) show small to large non-shaped particle sizes of YZrF₇ prepared from YF₃ reactant. The particle size is in range of 2-4 µm.


Figure 6.1 Crystal structure of YZrF₇.



Figure 6.2 A fragment of the crystal structure of the two types of zig-zag -Y-F-Y-F- chains showing the disorder at F5 position.

 Table 6.1 Crystallographic data of YZrF7.

Empirical formula	YZrF ₇
Formula weight	313.13 g/mol
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /m
Unit cell dimensions	a = 6.019(3) Å,
	b = 5.645(3) Å,
	c = 8.142(4) Å
	α = 90°, β = 103.373(7)°, γ = 90°
Volume	269.1(2) Å ³
Z	2
Density (calculated)	3.864 g/cm ³
Absorption coefficient	12.730 mm ⁻¹
Max. and min. transmission	0.7848 and 0.5686
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	648 / 0 / 52
Goodness-of-fit on F2	1.052
Final R indices [I>2σ(I)]	R1 ^a = 0.0341, wR2 ^b = 0.0895
R indices (all data)	R1 = 0.0352, wR2 = 0.0909

^a R1= $\Sigma(|F_0|-|F_c|) / \Sigma |F_0|$ ^b wR2 = $[\Sigma \{w(F_0^2-F_c^2)\}^2 / \Sigma wF_0^2]^{1/2}$

Atom	Wyckoff	Х	у	Z	U (eq)	Occupancy
	sites					
Zr	4f	0.8163(1)	0.2500	0.7271(1)	0.006(1)	1
Y	4f	0.6526(1)	0.2500	0.1857(1)	0.006(1)	1
F(1)	4f	0.7554(7)	0.2500	0.4753(5)	0.016(1)	1
F(2)	4f	0.8648(7)	0.2500	0.9783(5)	0.011(1)	1
F(3)	4f	0.0602(7)	0.0104(8)	0.7376(5)	0.037(1)	1
F(4)	4f	0.5876(9)	0.9949(11)	0.7162(5)	0.066(2)	1
F(5)	4f	0.4396(10)	0.0785(11)	0.9700(7)	0.011(1)	0.5

Table 6.2 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for YZrF₇. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1/2,z ; #2 -x+1,-y,z; #3 -x+1,y+1/2,-z; #4 -x+2,y+1/2,-z+1;

#5 -x+2,-y,-z+1; #6 -x+1,-y,-z+1; #7 -x+1,y+1/2,-z+1; #8 x,y,z-1; #9 x,y,z+1.

Table 6.3 Anisotropic displacement parameters (\AA^2) for YZrF₇. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2h \text{ k} a^* b^* U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U ¹³	U^{12}
Zr	0.006(1)	0.005(1)	0.005(1)	0	0.002(1)	0
Y	0.008(1)	0.006(1)	0.005(1)	0	0.002(1)	0
F(1)	0.015(2)	0.028(3)	0.006(2)	0	0.000(2)	0
F(2)	0.014(2)	0.013(2)	0.006(2)	0	0.003(2)	0
F(3)	0.059(3)	0.041(3)	0.016(2)	0.012(2)	0.018(2)	0.043(2)
F(4)	0.085(4)	0.107(5)	0.011(2)	-0.018(2)	0.018(2)	-0.092(4)
F(5)	0.014(3)	0.008(3)	0.011(3)	-0.003(2)	0.002(2)	-0.006(2)

Zr(1)-F(4)	1.980(4)	Y(1)-F(5)#1	2.150(6)	Y(1)-F(1)	2.295(4)
Zr(1)-F(4)#1	1.980(4)	Y(1)-F(5)#2	2.242(6)	Y(1)-F(2)#8	2.341(4)
Zr(1)-F(3)#1	1.983(4)	Y(1)-F(5)#3	2.242(6)	F(2)-Y(1)#9	2.341(4)
Zr(1)-F(3)	1.983(4)	Y(1)-F(3)#4	2.245(4)	F(3)-Y(1)#5	2.245(4)
Zr(1)-F(1)	1.997(4)	Y(1)-F(3)#5	2.245(4)	F(4)-Y(1)#6	2.275(4)
Zr(1)-F(2)	1.998(4)	Y(1)-F(4)#6	2.275(4)	F(5)-F(5)#2	1.178(12)
Y(1)-F(5)	2.150(6)	Y(1)-F(4)#7	2.275(4)	F(5)-Y(1)#2	2.242(6)
F(4)-Zr(1)-F(4)#1	93.3(4)		F(5)#2-Y(1)-F(3)#	5 71.9(2)	
F(4)-Zr(1)-F(3)#1	176.3(3)		F(5)#3-Y(1)-F(3)#	5 140.60(18)	
F(4)#1-Zr(1)-F(3)#	1 90.3(3)		F(3)#4-Y(1)-F(3)#	5 81.8(3)	
F(4)-Zr(1)-F(3)	90.3(3)		F(5)-Y(1)-F(4)#6	72.89(19)	
F(4)#1-Zr(1)-F(3)	176.3(3)		F(5)#1-Y(1)-F(4)#	6 104.7(2)	
F(3)#1-Zr(1)-F(3)	86.0(3)		F(5)#2-Y(1)-F(4)#	6 66.5(2)	
F(4)-Zr(1)-F(1)	89.61(1	5)	F(5)#3-Y(1)-F(4)#	6 127.4(2)	
F(4)#1-Zr(1)-F(1)	89.61(1	4)	F(3)#4-Y(1)-F(4)#	6 144.23(13)	
F(3)#1-Zr(1)-F(1)	90.15(1	4)	F(3)#5-Y(1)-F(4)#	6 90.9(2)	
F(3)-Zr(1)-F(1)	90.15(1	4)	F(5)-Y(1)-F(4)#7	104.7(2)	
F(4)-Zr(1)-F(2)	88.93(1	4)	F(5)#1-Y(1)-F(4)#	7 72.89(19)	
F(4)#1-Zr(1)-F(2)	88.93(1	4)	F(5)#2-Y(1)-F(4)#	7 127.4(2)	
F(3)#1-Zr(1)-F(2)	91.40(1	4)	F(5)#3-Y(1)-F(4)#	66.5(2)	
F(3)-Zr(1)-F(2)	91.40(1	4)	F(3)#4-Y(1)-F(4)#	7 90.9(2)	
F(1)-Zr(1)-F(2)	177.87(1	7)	F(3)#5-Y(1)-F(4)#	7 144.23(13)	
F(5)-Y(1)-F(5)#1	53.5(3)		F(4)#6-Y(1)-F(4)#	7 74.8(4)	
F(5)-Y(1)-F(5)#2	31.0(3)		F(5)-Y(1)-F(1)	143.82(17)	
F(5)#1-Y(1)-F(5)#2	2 83.55(9	9)	F(5)#1-Y(1)-F(1)	143.82(17)	
F(5)-Y(1)-F(5)#3	83.55(9	9)	F(5)#2-Y(1)-F(1)	123.62(15)	
F(5)#1-Y(1)-F(5)#3	3 31.0(3)		F(5)#3-Y(1)-F(1)	123.62(15)	
F(5)#2-Y(1)-F(5)#3	3 111.6(3)		F(3)#4-Y(1)-F(1)	72.96(12)	
F(5)-Y(1)-F(3)#4	142.87(1	8)	F(3)#5-Y(1)-F(1)	72.96(12)	
F(5)#1-Y(1)-F(3)#4	4 102.0(2)		F(4)#6-Y(1)-F(1)	71.42(13)	
F(5)#2-Y(1)-F(3)#4	4 140.60(1	8)	F(4)#7-Y(1)-F(1)	71.42(13)	
F(5)#3-Y(1)-F(3)#4	4 71.9(2)		F(5)-Y(1)-F(2)#8	74.48(18)	
F(5)-Y(1)-F(3)#5	102.0(2)		F(5)#1-Y(1)-F(2)#	8 74.48(18)	
F(5)#1-Y(1)-F(3)#	5 142.87(1	8)	F(5)#2-Y(1)-F(2)#	8 72.36(16)	

Table 6.4 Bond lengths (Å) and angles (°) for YZrF₇.

72.36(16)	Zr(1)-F(2)-Y(1)#9	139.8(2)
71.77(12)	Zr(1)-F(3)-Y(1)#5	166.7(2)
71.77(12)	Zr(1)-F(4)-Y(1)#6	156.6(2)
138.63(15)	F(5)#2-F(5)-Y(1)	78.8(5)
138.63(15)	F(5)#2-F(5)-Y(1)#2	70.2(5)
132.74(15)	Y(1)-F(5)-Y(1)#2	149.0(3)
175.1(2)		
	72.36(16) 71.77(12) 71.77(12) 138.63(15) 138.63(15) 132.74(15) 175.1(2)	72.36(16) $Zr(1)-F(2)-Y(1)#9$ $71.77(12)$ $Zr(1)-F(3)-Y(1)#5$ $71.77(12)$ $Zr(1)-F(4)-Y(1)#6$ $138.63(15)$ $F(5)#2-F(5)-Y(1)$ $138.63(15)$ $F(5)#2-F(5)-Y(1)#2$ $132.74(15)$ $Y(1)-F(5)-Y(1)#2$ $175.1(2)$



Figure 6.3 XRD patterns of the YZrF₇ with various reactants and dopants. a) Experimental from 10° - 60° . b) Experimental from 21° - 23° (YF₃ reactant). c) Calculated pattern based on the single crystal structure of undoped YZrF₇.



Figure 6.4 SEM images of YZrF7.



Figure 6.5 Average brightness of $YZrF_7:Er^{3+}$ under 980 nm excitation at room temperature (PMT = 100 V).



Figure 6.6 Average brightness of YZrF₇: Yb³⁺, Er^{3+} (2% and 10%) under 980 nm excitation (PMT = 50 V).

6.3.3 Photoluminescence properties

6.3.3.1 Brightness

 $YZrF_7$: Er^{3+} and $YZrF_7$: Yb^{3+} , Er^{3+} samples are used YF_3 as a reactant, and measured the average brightness of all visible emissions to figure out optimum concentration of Er^{3+} and Yb^{3+} doping. $YZrF_7$: Ln^{3+} (Ln = Eu, Tb, Er, Yb/Er) samples are also investigated absorption and emission spectra.

The brightness of YZrF₇:Er³⁺, YZrF₇:Yb³⁺, 2%Er³⁺, and YZrF₇:Yb³⁺, 10%Er³⁺ samples are shown in Figs. 6.5 and 6.6, respectively. All samples exhibit green light emission at room temperature under 980 nm excitation. The brightness of samples doped only Er³⁺ increases as the higher concentration of %Er³⁺ up to 10% before decreases due to the interaction between Er³⁺ neighboring, resulting in concentration quenching of Er³⁺ [13]. Co-doping of 1-25%Yb³⁺/10%Er³⁺ causes lower brightness than that of only Er³⁺ doping. However, the co-doping of 10-30%Yb³⁺/ 2%Er³⁺ shows significant increase in brightness – higher brightness than the samples doping only Er³⁺ and co-doping Yb³⁺/10%Er³⁺. The optimal concentration is found to be at 25%Yb³⁺/2%Er³⁺, before a concentration quenching of Yb³⁺ causing decrease in the brightness [13].

Results of low concentration of Er^{3+} and high concentration of Yb^{3+} exhibiting the highest brightness can be explained by Yb^{3+} - Er^{3+} up-conversion process (Fig. 6.7). At the 980 nm excitation, the excitation for Yb^{3+} : ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ contains the full f-f oscillator strength, whereas, the Er^{3+} : ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$ transition contains only a part of the oscillator strength [1]. In addition, the Yb^{3+} has higher an absorption coefficient than Er^{3+} at 980 nm [14]. Hence, at room temperature, the majority absorption specie will be Yb^{3+} before an energy transfer to Er^{3+} : ${}^{4}I_{11/2}$, and ${}^{4}G_{11/2}$ levels. High concentration of Er^{3+} depopulates excited photons in the Yb^{3+} - Er^{3+} up-conversion system. The co-doping between Yb^{3+}/Er^{3+} exhibits higher brightness than only Er^{3+} doping because that process as well.



Figure 6.7 Modified energy diagram of Yb³⁺ and Er³⁺ showing up-conversion process [12]. The colored downward arrows denote strong up-conversion emissions that lie in the visible spectral range. The dotted upward arrows on Er^{3+} (gray) and Yb³⁺ (black) describe strong excited state absorption steps, and the dotted downward arrows indicate non-radiative relaxation steps. The black dotted arrowed from Yb³⁺ to Er^{3+} indicate energy transfer steps that may occur in co-doped systems.



Figure 6.8 Average brightness of $YZrF_7$: 25%Yb³⁺, 2%Er³⁺ samples in YF₃, Y₂(C₂O₄)₃·9H₂O (YOXL), and Y₂O₃ as Y source. Measurements were performed under 980 nm excitation at room temperature (PMT = 50 V).

The average brightness magnitudes of YZrF₇: 25%Yb³⁺, 2%Er³⁺ with different of Y sources was in order of YF₃ > Y₂(C₂O₄)₃·9H₂O > Y₂O₃ (Fig. 6.8). At high temperature yttrium oxalate decomposes to be very small Y₂O₃ particles nearly atomic scale, which have higher reactivity than commercial Y₂O₃ containing mostly microsized particles. Comparing YF₃ vs. Y₂O₃, clearly YF₃ is preferable in diffusion reaction in solid state synthesis; it introduces F⁻ ions directly and its structure with 8 coordination of Y³⁺ similar to that of YZrF₇ structure, while Y₂O₃ has to be pushed more energy and time to generate YF₃ from reaction with HF gas produced from NH₄F decomposition.

6.3.3.2 Diffuse absorption spectra and emission spectra

 $YZrF_7$: Ln³⁺ (Ln = Eu, Tb, Er, Yb/Er) samples are investigated absorption and emission spectra. Diffuse reflectance technique is used to measure absorption spectrum of a sample powder [15-16]. In this work, the absorption spectra were calculated by plotting energy in wavelength *vs.* modified Kubelka-Munk function [17-19]:

$$F(R) = (1-R)^2/2R = k/s$$
 (Eq. 6.1)

where, R = reflectivity corrected from $R_{sample}/R_{standard}$, k = absorption coefficient and s = scattering coefficient.



Figure 6.9 a) Diffuse absorption spectra of YZrF₇: 10%Eu³⁺ b) Emission spectra of YZrF₇: 10%Eu³⁺ under 396 nm excitation (PMT = 500V).

6.3.3.2.1 YZrF₇:Eu³⁺

The diffuse absorption and emission spectra of YZrF₇: Eu³⁺ are demonstrated in Fig. 6.9. The diffuse absorption spectrum shows only major characteristic absorption of Eu³⁺ at 396 nm (strongest): ${}^{4}F_{0} \rightarrow {}^{5}L_{6}$ and 465 nm: ${}^{4}F_{0} \rightarrow {}^{5}D_{2}$. Some peaks can be observed in fluoride host at 320 nm (${}^{4}F_{0} \rightarrow {}^{5}H_{6}$), 365 nm (${}^{4}F_{0} \rightarrow {}^{5}D_{4}$), and 384 nm (${}^{4}F_{0} \rightarrow {}^{5}G_{2}$) [20]. The absorption under 396 nm excitation is considered as the strongest excitation level to use for measurement of emission spectrum of Eu³⁺ shown in Fig. 6.9b. The sample shines orange-red light under UV excitation. The strong emission peaks correspond to transitions from ${}^{5}D_{0}$ level to the ${}^{7}F_{J}$ (J = 0, 1, 2, 3, 4) since the ${}^{5}D_{0}$ (J = 0) level will not be splitted by the crystal field, and the non-radiative transition from higher level to ${}^{5}D_{0}$ is pretty fast at room temperature [21]. However, it has been proposed that the radiative transition has to be 4-5 times of the maximum phonon frequency of the host lattices, resulting in weak radiative transitions from ${}^{5}D_{1}$ and ${}^{5}D_{2}$ to ${}^{7}F_{J}$ [21-22]. The

intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is dependent on the local symmetry of the Eu³⁺ [21]. In case of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ dominance (Fig. 6.9b), Eu³⁺ ions are located in the sites with inversion symmetry.



Figure 6.10 Diffuse absorption spectrum of YZrF₇:10%Tb³⁺. a) scanning in range of 300-400 nm b) zooming in range of 300-380 nm.



Figure 6.11 Emission spectra of $YZrF_7$: Tb³⁺ under 385 nm excitation (PMT = 500 V).

6.3.3.2.2 YZrF₇:Tb³⁺

The diffuse absorption spectrum (Fig. 6.10) shows the f-f transitions within Tb^{3+} . Only dominant and strongest peak is found at 385 nm: ${}^{7}\text{F}_{6} \rightarrow {}^{5}\text{D}_{3}$ with the other weak absorptions at 313 nm: ${}^{7}\text{F}_{6} \rightarrow {}^{5}\text{D}_{0}$, 357 nm: ${}^{7}\text{F}_{6} \rightarrow {}^{5}\text{D}_{2}$ and 373 nm: ${}^{7}\text{F}_{6} \rightarrow {}^{5}\text{G}_{6}$ [23]. The sample emits green light under 385 nm excitation, which is considered to be the highest excitation associated with the diffuse absorption result. The emission spectrum in Fig. 6.11 is obtained from the transition from ${}^{5}D_{4}$ level to the ground state ${}^{7}F_{J}$ (J = 3, 4, 5, 6). The strongest peak is from 546 nm: ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$.



Figure 6.12 Diffuse absorption spectrum of YZrF₇: 20%Er³⁺ from Er³⁺ ground state ${}^{4}I_{15/2}$.



Figure 6.13 Diffuse absorption spectrum of $YZrF_7$: 25%Yb³⁺, 10%Er³⁺ a) Er³⁺ absorption peaks from ground state ${}^{4}I_{15/2}$. b) Yb³⁺ absorption.

6.3.3.3.3 YZrF₇:Er³⁺ and YZrF₇: Yb³⁺, Er³⁺

The diffuse absorption spectra of YZrF₇:Er³⁺ (Fig. 6.12) are associated to Er³⁺ absorption from the ground state ${}^{4}I_{15/2}$ transitions to excited states around 400-550 nm corresponding to ${}^{2}H_{9/2}$, ${}^{4}F_{5/2}$, ${}^{4}F_{7/2}$, ${}^{2}H_{11/2}$ (strongest), and ${}^{4}S_{3/2}$ levels [24]. The similar Er³⁺ absorption peak patterns were also found in YZrF₇: 25%Yb³⁺, 10%Er³⁺ (Fig. 6.13a). Yb³⁺

absorption (Fig. 6.13b) is a broad peak from 972-980 nm, and centered around 976 nm corresponding to the transition from ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$. This peak is usually broad at room temperature, therefore, the peak base will be narrower within 3-4 nm of based-width at low temperature measurement below 77 K [12, 25].



Figure 6.14 a) Emission spectra of $YZrF_7$: Er^{3+} (PMT = 200 V) b) Emission spectra of $YZrF_7$: Yb^{3+} , 2% Er^{3+} (PMT = 100 V). Measurements were performed under 980 nm excitation.

The emission spectra of YZrF₇: Er^{3+} (Fig. 6.14a) and YZrF₇: Yb³⁺, 2% Er^{3+} (Fig. 6.14b) under 980 nm excitation exhibit green light composing of a combination of blue, green ,and red because of the Er^{3+} absorption (see Fig. 6.7), corresponding to the transition from ${}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$ (blue), ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ (green), ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ (green, strongest) and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ (red) [12]. The emission spectra results agree with the brightness results; the blue, green and red emissions increase as the higher Er^{3+} doping up to 10% Er^{3+} and 25%Yb³⁺/ 2% Er^{3+} , before decreasing when concentration of dopants are higher than that of the optimal one. The red emission enhances significantly as increase in %Yb³⁺ doping, then decrease when passing the optimal concentration. Because the distance between Yb³⁺ and Er^{3+} ions becomes shorter as more Yb³⁺ ions being in the host structure, resulting in energy back transfer from Er^{3+} to Yb³⁺ ions. The cross-relaxation diminishes population in ${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$ levels, and raise the population in ${}^{4}F_{9/2}$ level [13]. Hence, at very high

concentration of Yb^{3+} , e.g. $30\% Yb^{3+}$, the red emission even becomes higher than green emission.



Figure 6.15 Emission spectra of NaYF₄: 18%Yb³⁺, 2%Er³⁺ (blue line) and YZrF₇: 25%Yb³⁺, 2%Er³⁺ (red line). Measurements were performed under 980 nm (PMT = 100 V).

Fig. 6.15 demonstrates a comparison of emission spectra between optimum doping Yb³⁺ and Er³⁺ for YZrF₇, and hexagonal NaYF₄. NaYF₄: Yb³⁺, Er³⁺ have much more green emissions (at 525 nm and 548 nm), slightly more red emission (657 nm), but less blue (412 nm) emission than those of YZrF₇:Yb³⁺, Er³⁺. Net emissions of NaYF₄:Yb³⁺, Er³⁺ exhibit better up-conversion luminescence. It could be corresponded to low phonon energy of NaYF₄ (360 cm⁻¹) [12]. As the bond distance decreases, the phonon energy of the bond will be increased. Yb³⁺ and Er³⁺ will be substituted in Y³⁺ rather than Zr⁴⁺ because of larger size of Y³⁺. In case of NaYF₄, Yb³⁺ and Er³⁺ are also in Y³⁺ sites. So it can be used an average Y³⁺-F⁻ distance representing distances between lanthanide ions and F⁻ ions. The average bond distances between Y³⁺-F⁻ are 2.183 Å for YZrF₇, and 2.351 Å for NaYF₄ [4]. Consequently, YZrF₇ has higher phonon energy because of shorter bond length between atoms to lanthanide centers, resulting in lower up-conversion efficiency.

6.4 Summary

The YZrF₇ powder samples are synthesized by solid state reactions with particle size around 2-4 µm. The single crystal is grown and structural refined in monoclinic P2₁/m with lattice parameters: a = 6.019(3) Å, b = 5.645(3) Å, c = 8.142(4) Å, $\alpha = 90^{\circ}$, $\beta = 103.373(7)^{\circ}$, and $\gamma = 90^{\circ}$. The photoluminescent properties of YZrF₇ are investigated through doping Eu³⁺, Tb³⁺, and Er³⁺. It can be a candidate host for up-conversion phosphor when co-doping with Yb³⁺ and Er³⁺. The optimal concentrations are found at 10%Er³⁺ alone, and 25%Yb³⁺/2%Er³⁺ co-doping. Although, this host shows lower intensity of emission than that of well-known hexagonal NaYF₄: 18%Yb³⁺, 2%Er³⁺, it is established as a new phosphor host, and can be expanded study in the other application e.g. a pump laser host when doping with Nd³⁺.

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Chapter 7

Conclusion

This dissertation focused and presented a couple groups of earth-abundant materials for PV absorbers together with a new luminescent host from lanthanide fluoride. Olivine Fe₂(Si, Ge)S₄ were proposed as a PV absorber candidates. In Fe₂GeS₄, band gap energy was found to be 1.4-1.45 eV consistent in bulk, thin film and single crystal samples. Fe₂GeS₄ thin film demonstrated high absorption, $\alpha > 10^5$ cm⁻¹ within Eg+1 eV, and *p*-type semiconducting of Fe₂GeS₄ with estimated carrier concentration of 10^{18} cm⁻³. Those properties as well as capability of band gap adjusting via solid-solutions provided advantages and promising Fe-based PV absorber candidates.

Exploration of new Cu-based solar absorbers which are comparable to CIGS were deployed in Cu_3 -V-VI₄ system, where V = P, As, Sb, and VI = S, Se. Optical band gaps of enargite $Cu_3PS_{4x}Se_x$ ($0 \le x \le 4$) compounds were found to be range from 2.36 eV (x = 0) to 1.35 eV (x = 4). Electrical measurements of pressed pellets established p-type semiconducting with hole carrier concentrations in range of 10¹⁶-10¹⁷ cm⁻³. Similar optical and electrical properties were also observed in $Cu_3P_xAs_{1-x}S_4$ ($0 \le x \le 1$) compounds; optical band gap range from 2.36 eV (x =1) to 1.3 eV (x =0), p-type semiconductivity with 10^{15} - 10^{16} cm⁻³ of carrier concentrations. Although, Cu₃P_xSb_{1-x}S₄ (0 ≤ x ≤ 1) system did not form solid solutions, $Cu_3As_xSb_{1-x}S_4$ ($0 \le x \le 1$) system was reported in the literature, and famatinite Cu₃SbS₄ band gap was found to be 0.9 eV; providing opportunity for band gap tuning in range of 0.9-1.3 eV. Recently, electronic structure calculation of Cu_3PSe_4 demonstrated similar absorption property to that of CIGS. Supported by computational calculation result, Cu₃-V-VI₄ becomes interesting and promising system that provides wide range of band gap with excellent electrical property, and encourages further research and development as a novel class of Cu-based absorber candidates for both single and multijunction PV cell, and solar fuel generation.

The recently rise of $Cu_2ZnSn(S, Se)_4$ research as PV absorbers leaded to our discovery of a new quaternary $CuZnPS_4$ as a defect structure of Cu_3PS_4 . It crystallized in a non-centrosymmetric space group I-4; a = b = 5.4939(7) Å, c = 9.233(2) Å. $CuZnPS_4$ exhibited second harmonic generation, a non-linear optical property. Optical property of

 $CuZnPS_4$ and Cu_3PS_4 were quite similar, but unlikely Cu_3PS_4 , which shows electrical semiconducting, $CuZnPS_4$ were highly electrical insulation.

A new lanthanide fluoride host, YZrF₇ crystallized in space group P2₁/m with lattice parameters: a = 6.019(3) Å, b = 5.645(3) Å, c = 8.142(4) Å, $\alpha = \gamma 90^{\circ}$, and $\beta = 103.373(7)^{\circ}$. The luminescent properties, when doping with Eu³⁺, Tb³⁺, Er³⁺ and co-doping Yb³⁺ and Er³⁺, were investigated as a new green up-conversion host. The optimal concentration of dopants in this host were found at 10%Er³⁺ and co-doped 25%Yb³⁺ and 2%Er³⁺.

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Appendices

Appendix A

Solution processing of Cu₃PSe₄ thin films

Cu₃PSe₄ thin films were obtained via solution processing of Cu-precursors following annealing films with P and Se in evacuated, sealed fused silica tubes. Cuprecursor films were prepared by spin-coating of aqueous 0.25 M of Cu(HCOO)₂·4H₂O (98%, Alfa Aesar) solution on clean 1" x 1" fused silica substrates (GM Associates, Inc.) at 3000 rpm for 1 min. Spun films were heated at 150°C for 1 min, then annealed in evacuated sealed tube with 1.5 mmol of P (99.999+%, Materion Advanced Chemicals) and 5.1 mmol of Se (99.999%, Alfa Aesar) powder for 3 h at 480 °C. Film samples were identified by X-ray diffraction (XRD) utilizing Cu Kα radiation on a Rigaku Rapid diffractometer, and obtained XRD patterns of Cu₃PSe₄ (Fig. A.1) with major peaks position and intensity in good agreement with a reference ICSD# 95412. A broad peak around 20 of 15-25° was from the amorphous substrate.



Figure A.1 XRD pattern of Cu₃PSe₄ thin film deposited on fused silica substrate.

Optical transmission and reflection of thin films were collected from a spectrometer based on Ocean Optics HR4000 UV-VIS detector with a DH-2000-BAL balanced deuterium/tungsten halogen source. An absorption coefficient (α) was calculated from Eqs. A.1 and A.2 [1]:

T = (1-R)
$$e^{-\alpha t}$$
 (Eq. A.1)
thus, α = - [ln(T/1-R)]/t (Eq. A.2)

where, T = transmission, R = reflection and t = thickness of sample



Figure A.2 Optical absorption of a ~50 nm Cu₃PSe₄ film.

An onset of absorption was found to be 1.35-1.4 eV (Fig. A.2), in good agreement with a calculated band gap (1.38 eV) [2]. This film deposition method was able to make Cu₃PSe₄ thin films, however, it showed low reproducibility. The typical problems were found, i.e., bad adhesion of material on fused silica substrate, volatility of P resulting in secondary phases such as Cu₂Se, CuSe, Cu₇PSe₆, possibility of finding small amount of copper oxides formation via heating film in air and not seen in XRD patterns. Suggested methods for film quality improvement include spin-coating and film treatment in inert atmosphere, Cu-P-Se solution via hydrazine/hydrazine hydrate approach [3], Closed space vapor transportation (CSVT) [4].

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Appendix B

MPS_3 (M = Mn, Fe, Co, Ni, Zn, Sn)

A survey of band gap of layered structure (Fig. B.1) of monoclinic MPS₃ (M = Mn, Fe, Co, Ni, Zn) including framework structure of monoclinic SnPS₃ or Sn₂P₂S₆ (Fig. B.2). Photoelectrochemical measurement on single crystals of FePS₃ and NiPS₃ showed *p*-type conductivity, whereas SnPS₃ were *n*-type conductivity [1].



Figure B.1 (Mn, Fe, Co, Ni, Zn)PS₃ structure (space group C2₁/m). M^{2+} is represented in red balls/polyhedral. P is illustrated in greenballs/polyhddra. S²⁻ is shown in yellow ball. [MS₆] units are edge sharing separated with alkane-liked [S₃P-PS₃] units.



Figure B.2 SnPS₃ or Sn₂P₂S₆ structure (space group P2₁/c). P⁴⁺ is represented as green balls/polyhedra. Sn²⁺ is illustrated in grey balls/polyhedra. S²⁻ is shown in yellow ball.

Powder samples of MPS₃ were prepared by solid state reaction of corresponding mixtures elemental powders; Mn (99.95%, Alfa Aesar), Fe (99.9998%, Alfa Aesar), Co (99.8%, Cerac), Ni (99.9%, Cerac), Zn (99.9%, Cerac), Sn (99.99%, Cerac), P (99.9999+%, Alfa Aesar), and S (99.9995%, Alfa Aesar). The reactants were transferred to evacuated sealed fused silica tubes, and heated at 550 °C for 24 h. Powder X-ray diffraction data were collected with a Rigaku Ultima IV diffractometer by using Cu Kα radiation. Optical band gaps were estimated from diffuse-reflectance measurements. Light was directed onto the sample from a DH-2000-BAL balanced deuterium/tungsten halogen source and detected with an Ocean Optics HR4000 UV-VIS spectrometer. MgO powder (99.95%, Cerac) was used as a reference. Band gap measured from diffuse reflectance was summarized in Table B.1.

	-	-	
Compound	Powder	Band gap	Comment
	color	(eV)	
MnPS ₃	green	~2.5	2 onsets of absorption similar to Mn(S,Se),
			where the 1^{st} one turned on ~1.6 eV, and 2^{nd}
			one (strongest) ~2.5 eV.
FePS ₃	black	~0.6	Ambiguous 1.3 eV of E _g
CoPS ₃	black	<0.6	Below detection limit of detector
NiPS ₃	black	<0.6	Below detection limit of detector
ZnPS ₃	white	3.3	-
SnPS₃	yellow	2.3	-

Table B.1 Band gap energy of MPS_3 estimated from diffuse reflectance measurement.

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Appendix C

Tetrahedrite (Cu, Zn)₁₂Sb₄(S, Se)₁₃

Natural mineral tetrahedrite [1] $(Cu^+, Ag^+)_{10}(Cu^{2+}, Zn^{2+}, Fe^{2+}, Hg^{2+})_2(As^{3+}, Sb^{3+})_4(S, Se)_{13}$ is one of a very few 3-dimensional framework Cu-Zn chalcogenides, that exist and are reported up to nowsday. Synthetic tetrahedrite $Cu_{12}Sb_4S_{13}$ (Cubic, space group I-43m) was investigated temperature dependent crystal structure [2]. Nevertheless, band gap determination of synthetic $Cu_{12}Sb_4S_{13}$ and $Cu_{10}Zn_2Sb_4S_{13}$ has not been reported.

Powder samples were prepared by solid state reaction of corresponding mixtures elemental powders; Cu (99.999%, Alfa Aesar), Zn (99.9%, Cerac), Sb (99.9999%, Alfa Aesar), S (99.9995%, Alfa Aesar), and Se (99.999%, Alfa Aesar). The reactants were transferred to evacuated sealed fused silica tubes, and heated at 500 °C for 24 h. Additional regrinding and reheating were required several times to obtain single phase. Powder X-ray diffraction data were collected on a Rigaku Ultima IV diffractometer by using Cu K α radiation. Only Cu₁₀Zn₂Sb₄Se₁₃ samples contained small amount of ZnSe phase, and the samples were not done electrical measurements.

Single crystal growth of $Cu_{10}ZnSb_4S_{13}$ via chemical vapor transport using NH₄Br (99.999%, Alfa Aesar) as a flux agent was attempted, and obtained samples crystallized in cubic unit cell system. Lattice parameters (at 173 K) were, a = 11.061(2) Å and V =1353.2(4) Å³. For comparison, lattice parameter of $Cu_{12}Sb_4S_{13}$ at 295K was, a = 10.2393(6) Å, V = 1102.1(2) Å³ [2]. Structure refinement from those crystals has been working with an assigned crystal code name "dk58".

Optical band gaps of powder samples were measured from diffuse reflectance. Light was directed onto the sample from a DH-2000-BAL balanced deuterium/tungsten halogen source and detected with an Ocean Optics HR4000 UV-VIS spectrometer. MgO powder (99.95%, Cerac) was used as a reference. Onsets of absorption spectra of $Cu_{10}Zn_2Sb_4(S, Se)_{13}$ (Fig. C.1) occurred ~1.7 eV in sulfide and ~1.4 eV in selenide. The presence of Zn^{2+} in tetrahedrite structure increased band gap significantly from $Cu_{12}Sb_4S_{13}$

; < 0.5 eV, below detection limit of the instrument. Fe^{2+} substitution in place of Zn^{2+} exhibited low energy gap below the detection limit of the instrument.



Figure C.1 Absorption spectra of $Cu_{10}Zn_2Sb_4S_{13}$ (black line) and $Cu_{10}Zn_2Sb_4Se_{13}$ (red line) collected from diffuse reflectance measurements.

Room temperature resistivity of $Cu_{10}Zn_2Sb_4S_{13}$ were measured on 0.5" pressed pellets (~80% of theatrical density) by employing the van der Pauw geometry on a LakeShore 7504 measurement system. Majority-carrier type was determined from Seebeck measurements on an custom-built system by applying a 3 °C temperature gradient to the samples. Pressed pellets of $Cu_{10}Zn_2Sb_4S_{13}$ demonstrated +470 to +530 μ V/K indicating *p*-type semi-conducting characteristic, in good agreement with resistivity of 9-10 Ω cm.

The optimized synthesis condition for $Cu_{10}Zn_2Sb_4Se_{13}$ is necessary to prevent ZnSe crystallization, and further investigate electrical property. Thermal gravimetric analysis (TGA) is recommended to identify thermal stability in tetrahedrite compounds, and the crystallization temperatures of ZnS and ZnSe.

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Appendix D

Preparation of $Bi_{1-x}Ca_xCuOSe$ ($0 \le x \le 0.06$) targets

MCuOQ (M = La, Bi; Q = S, Se, Te) is a layered structure of oxide-chalcogenide, which has been found unique optoelectronic properties [1]. Small amount of Ca²⁺ substitution into Bi³⁺ sites of BiCuOSe (E_g ~0.85 eV [2]) exhibits *p*-type conductivity [3]. This section provided a preparation of Bi_{1-x}Ca_xCuOSe target for pulsed laser deposition (PLD). The methodology was modified from [4] with an improvement of target density up to 87% of its theoretical value.

Powder samples were prepared by solid state reaction of corresponding reactants; Bi (99.5%, Cerac), Bi₂O₃ (99.9995%, Alfa Aesar), Cu2Se (99.5%,Cerac), Se (99.95%, Cerac), and CaO (99.95%, Alfa Aesar). The reactants were transferred to evacuated sealed fused silica tubes, and heated at 500 °C for 12 h. Additional regrinding and reheating were done at the same reaction temperature for 12 h. Powder X-ray diffraction data were collected with a Rigaku Miniflex II diffractometer utilizing Cu Kα radiation. All samples were reground to be very fine powder, pressed at 4 tons (room temperature) to obtain 1" diameter pellets, and then sintered at 850 °C for 3 h under 5000 psi of Ar (g) in a hot isostatic press (American Isostatic Presses, Inc. AIP6-30H). Final density of targets was 85-87% of theoretical value.

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