

Energy needs have grown with the population, economy, and technology. The International Energy Agency (IEA) predicts a 25% increase in global energy demand by 2040. Photovoltaic and thermoelectric waste energy collecting may be able to meet this growing demand in a sustainable manner. For 2022, the International Renewable Energy Agency (IRENA) estimates 1053 GW of solar PV capacity (*International Renewable Energy Agency, 2023*). With thermoelectric technology, waste heat may be used to generate power, improving energy consumption. These sources diversify energy portfolios and lessen reliance on fossil fuels, but their development relies heavily on novel materials with abundant earth resources and promising material prospects. Understanding the optoelectronic, mechanical, and thermal properties of diverse materials and their device modeling is an important subject of study for building highly efficient energy devices.

1.1 Chalcogenides and their evolution

Starting with Silicon, the semiconductor industry has gone through several stages of revolution and discovery in both technology and materials (Figure 1.1). Chalcogenides, which have one chalcogen anion and one electropositive element, have long been explored and employed in electrical and optical devices such as displays, sensors, and sophisticated integrated systems (Hadke et al., 2022). Several semiconductor branches derive from the group IV element Si in seeking energy applications such as photovoltaics. In this domain, numerous combinations such as III-V (GaAs), II-VI (PbTe, CdSe, CdTe), and I-III-VI₂ (CuInS₂, CuGaSe₂) have been established to maintain charge neutrality. When compared to conventional silicon-based devices, these multinary chalcogenides are highly suited for thin film technology-based devices due to lower material and processing costs and more material flexibility (Saparov, 2022).

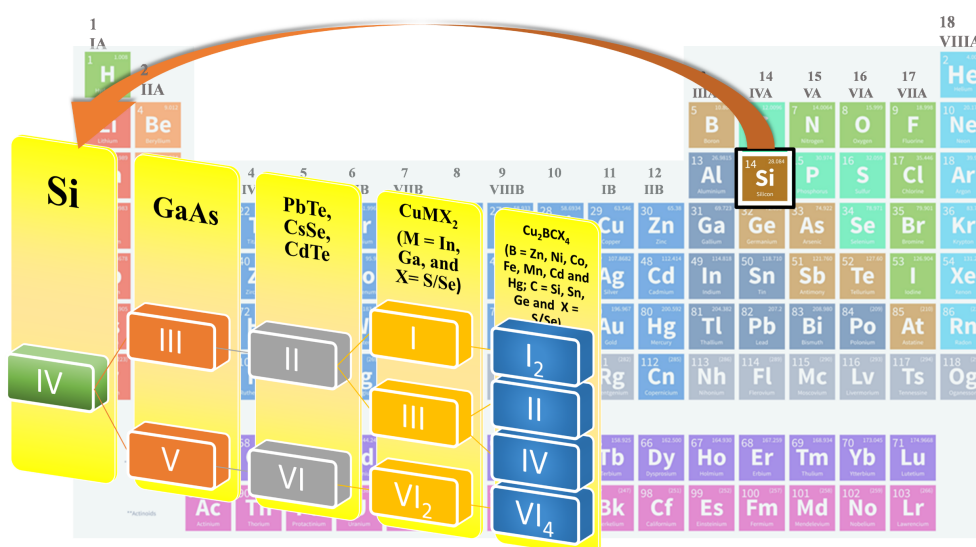


Figure 1.1 Evolution of Multinary Chalcogenides. Starting from Si, the Binary, ternary and quaternary chalcogenides are prepared using multiple group elements

1.2 Cu-based Chalcogenides for Photovoltaic and Thermoelectric

Chalcogenide appears to be a promising chemical space for the synthesis of new energy materials. Materials such as $\text{Cu}_2(\text{In,Ga})\text{Se}_2$, CdTe , $\text{Sb}_2(\text{SSe})_3$, $\text{AgBi}(\text{SSe})_2$, $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ and $\text{CuSb}(\text{S,Se})_2$ have emerged as major photo absorbers for reasons such as adequate band gap, high optical absorption, small effective masses for increased carrier mobility, and benign defects and grain boundaries (Hadke et al., 2022). The above-mentioned materials, as well as others such as ZnIn_2Te_4 , CuInTe_2 , Bi_2Se_3 , AgSbTe_2 , GeTe , PbSe , and SnSe , are being investigated for thermoelectric applications with the expectation of higher carrier mobility and decreased heat transmission (X. L. Shi et al., 2020). Only a handful of them, such as CdTe and CIGS for photovoltaics and PbTe and Bi_2Se_3 for thermoelectric devices, are commercially available. The fundamental problem limiting the commercialization of PV materials is unfavourable intrinsic point defects that cause carrier recombination and reduced carrier extraction (Susanne Siebentritt and Susan Schorr, 2012). On the other hand, the repeatability issue of the reported high ZT materials, as well as cost-effectiveness and scalability issues, are among the few limits that point to additional research into efficient thermoelectric materials.

Thin film technology, which is based on CdTe and CIGS solar cells, is propelling the PV market by allowing for low-cost and large-scale photovoltaic deployment. So far CdTe has a record efficiency of 22.1% (Green et al., 2018), whereas CIGS has a claimed efficiency of 23.35% (Chantana et al., 2020). CdTe and CIGS have carrier lifetimes of 30 ns and 100 ns, respectively. Despite having a lower efficiency and lifetime than Si (lifetime 1ms and efficiency 27%), these thin film technology with low-temperature and low-cost production seems viable for the PV market. Even with this advancement, CdTe still has certain downsides. The lower grain size induced lesser lifetime and hence grain boundary recombination, and the presence of toxic and scarce constituent elements are some of them. On the other side, due to the attractive optoelectronics feature of CIGS, it harnessed towards steady progress in developing CIGS-based flexible PV, tandem solar cells. Here, the excellent defect tolerance due to defect-defect interactions leading to long minority carrier lifetime and avoided deep defects make it beneficial compared to CdTe technology (J. S. Park et al., 2018; Unold & Schock, 2011). However, the scarcity of In in the earth's crust restricts the long-term competitiveness of CIGS solar cells. Quaternary kesterite $\text{Cu}_2\text{ZnSnS}_4$ -based solar cells have also been created in recent years. In this sequence, however, the most efficient CZTS and its alloy-based device have recorded 13.8% efficiency (P. Chen et al., 2023). Potential fluctuations and band tailing are caused by thermodynamically favourable antisite disorders such as Cu_{Zn} and Zn_{Cu} , ultimately lowering open circuit voltage and restricting device performance (S. Chen et al., 2013; Shin et al., 2017). The similar ionic size of Cu and Zn atoms is the primary cause of this antisite disorder, which is proposed to be addressed by multiple cation replacements like Ba, Hg, Sr, and Cd on the Zn site, producing more ionic size mismatch with Cu (Hong et al., 2016a). Considering the same, we will concentrate on Hg substitution and attempt to grasp the electronic structure calculations followed by deriving solar cell device metrics.

There is also a wealth of literature on high ZT materials. In compounds such as GeTe , PbTe , Cu_{2-x}Se , and Sn_{1-x}Se , $\text{ZT} > 2$ is predicted (X. L. Shi et al., 2020). These systems' intriguing phonon dynamics result in decreased thermal conduction for a narrow temperature range suited for applications. Many approaches, such as nano-structuring, alloying, and doping, are used to create high phonon scattering while maintaining low thermal conduction (Bin et al., 2023; Parashchuk et al., 2022; Qin et al., 2023; Wenyu Zhao et al., 2017). The introduction of the heavy constituent may also favour decreased heat conduction as dictated by the Keyes law (Keyes, 1959). Given the significance of chalcogenides and the potential influence of Hg atoms, we investigate the Hg-based quaternary chalcogenide $\text{Cu}_2\text{HgSnS}_4$ for thermoelectric applications.

1.3 Motivation

Cu-based quaternary compounds having the formula Cu_2BCX_4 (where B, C and X belongs to group II, group IV and S/Se/Te respectively) are emerging chalcogenide family for energy application as a few of them, such as $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{BaSnS}_4$ have been explored very well (Y. Kim et al., 2021); however, the other possible variation, cation substitutions are remaining to explore. Cu_2BCX_4 exhibits a diamond-like structure (DLS), which can be derived from the diamond silicon prototype via simple electron counting rules. Diverse chemistry observed in the DLS is fundamentally tied to the number of cation mutations that preserve tetrahedral coordination. $\text{Cu}_2\text{ZnSnS}_4$ -based solar cells have noticed Voc deficit issues among the most sought quaternary compounds. In order to deal with heavy cation substitution, Hg remains unexplored. The quaternary compound $\text{Cu}_2\text{HgSnS}_4$ remains in the stannite phase, unlike the most favorable kesterite phase in $\text{Cu}_2\text{ZnSnS}_4$ (Sarmadian et al., 2016). Additionally, due to the presence of this element deep inside the periodic table belonging to group II, its quaternary chalcogenides seem to have the potential for lower heat conduction. Due to all these facts, we preferred to investigate $\text{Cu}_2\text{HgSnS}_4$ from the aspect of photovoltaic and thermoelectric, which has yet to be explored.

1.4 Objectives

This work mainly focuses on the thorough analysis of optoelectronic, mechanical, and thermal prospects of the $\text{Cu}_2\text{HgSnS}_4$ and its selenium alloy for predicting their suitability for photovoltaics and thermoelectric applications. The key feature involved in this thesis are;

1. Detailed optoelectronic and Mechanical study of the pristine $\text{Cu}_2\text{HgSnS}_4$ and its alloy $\text{Cu}_2\text{HgSn}(\text{Se}_x\text{S}_{1-x})_4$.
2. Possibility of single and multiple junctions and graded bandgap solar cells.
3. Phonon dynamics with scattering insights in $\text{Cu}_2\text{HgSnS}_4$ for predicting the suitability of thermoelectric application.

1.5 Outline of the Thesis

The thesis provided here is heavily focused on the photovoltaic and thermoelectric properties of chalcogenides, revealing their fascinating physics. **Chapter 1** discusses the evolution of chalcogenides material. It also provides some insight into the energy application possibilities of Cu-based chalcogenides as well as their future potential. **Chapter 2** discusses the basics of Photovoltaics and Thermoelectrics along with the status of Cu-Chalcogenides materials for energy uses. **Chapter 3** covers the fundamentals of density function theory as well as transport properties and scattering mechanisms employed over subsequent chapters. **Chapter 4** describes the electronic structure and optical properties of $\text{Cu}_2\text{HgSnS}_4$, as well as the evolution of these properties with Sulfur and Selenium alloys. The single junction performance of the $\text{Cu}_2\text{HgSnS}_4$ absorber-based solar cell is described in **Chapter 5** utilizing drift-diffusion modelling and considering the input parameters as obtained in Chapter 1. It also demonstrates the superiority of graded bandgap solar cells over tandem junctions. The phonon dynamics in $\text{Cu}_2\text{HgSnS}_4$ are highlighted in **Chapter 6** using three phonon theory, including particle and wave-like treatment. The electron and hole scattering is also expressed here. The thermoelectric figure of merit is then predicted.