Curriculum 2. Mechanics, Materials, Chemistry and Energy

Muhammad Ubaidah Syafiq bin Mustaffa

Alternative Uses of CZTS Thin Films for Energy Harvesting



UNIVERSITY OF TRENTO

UNIVERSITY OF TRENTO - Italy Department of Civil, Environmental and Mechanical Engineering



Doctoral School in Civil, Environmental and Mechanical Engineering Topic 2. Mechanics, Materials, Chemistry and Energy - 33° cycle 2017/2020

Doctoral Thesis - September 2021

Muhammad Ubaidah Syafiq bin Mustaffa

Alternative Uses of CZTS Thin Films for Energy Harvesting

Supervisors Prof. Paolo Scardi Dr. Narges Ataollahi

Abstract

The search for renewable energy resources and ways to harvest them has become a global mainstream topic among researchers nowadays, with solar cells and thermoelectric generators among the energy harvesting technologies currently being researched in vast. CZTS (Cu₂ZnSnS₄), a p-type semiconducting material initially researched to replace copper indium gallium selenide (CIGS) as the light absorbing layer in thin film solar cells, was studied in this doctoral work for alternative uses in energy harvesting. This work aims to systemically investigate the prospects of CZTS to be used as hole transport layers and thermoelectric generators.

CZTS thin film was successfully fabricated using a versatile approach involving hot-injection synthesis of CZTS nanoparticles ink followed by spin coating and thermal treatment. Results obtained revealed the possibility to fine control CZTS thin film fabrication based on ink concentration and spin. Besides that, thermal treatment temperature was found to affect the film's overall properties, where an increase in thermal treatment temperature improved the degree of crystallinity and electrical properties. In addition, a phase change going from less stable cubic and wurtzite structures to a more stable tetragonal structure was also observed. Furthermore, CZTS was found to be a good candidate to replace the commonly used organic hole transport layer in perovskite solar cells, with potentials in improving performance and stability. In addition, CZTS also possessed good transport properties to be a potential p-type material in a thermoelectric generator, with the preliminary performance of fabricated CZTS/AZO thermoelectric generator showing a maximum power output of ~350 nW at ~170 K $\Delta T.$

These findings provide new perspectives for CZTS in energy harvesting applications, despite the struggle in its development as the absorber layer in thin film solar cells. Besides providing a deeper understanding of CZTS and its vast possibilities in energy harvesting applications, promising future research stemming from this work is also limitless, reinventing ways in material studies, in search of alternative applications which may be of benefit.

Index	Page			
Abstract	1			
Index	2			
Introduction	4			
 Solution-based synthesis and characterization of Cu₂ZnSnS₄ (CZTS) thin films 				
Abstract	15			
1.1. Introduction	16			
1.2. Results and discussion	17			
1.2.1.CZTS ink concentration and spin rate	17			
1.2.2.TT temperature	20			
1.3. Materials and methods	26			
1.3.1.Synthesis of CZTS Nanoparticles Ink	26			
1.3.2.Deposition of CZTS Thin Film	27			
1.3.3.CZTS Thin Film Characterization	27			
1.4. Conclusions	29			
2. Progress in CZTS as hole transport layer in perovskite	31			
Abstract	31			
2.1 Introduction	32			
2.1. Introduction 2.2. Current progress on Cu ₂ ZnSnS ₄ (CZTS) materials	52			
in perovskite solar cells	40			
2.3. Perspective	53			
2.4. Outlook	53			
 Thermoelectric generator (TEG) based on thin films of CZTS 	55			
Abstract	55			
3.1. Introduction	55			
3.2. Materials and methods	58			
3.2.1.Synthesis of CZTS nanoparticles ink	58			
3.2.2.CZTS thin film deposition and thermal	50			
treatment	39			
3.2.3.CZTS/AZO TEG fabrication	60			
3.2.4. Thin films characterization	61			
3.2.5.Thin film CZTS/AZO TEG performance measurement	62			
3.3. Results and discussion	64			

3.3.1.Morphological and structural characterization of CZTS thin film	64
3.3.2.Thermoelectric properties of SC CZTS thin film	67
3.3.3.Morphological and structural characterization of AZO thin film	71
3.3.4. Thermoelectric properties of AZO thin film	73
3.3.5.Thin film CZTS/AZO TEG preliminary performance analysis	74
3.3.6.Optimization of thin film CZTS/AZO TEG	77
3.4. Conclusions	80
4. Conclusions, perspectives, and ongoing activities	82
5. Appendix	90
5.1. List of publications	90
5.2. Participation to schools and conferences	90
References	91

Introduction

Energy availability has evolved over the course of humanity. In the beginning, traditional biomass from the burning of wood, crop waste, or charcoal was considered the main energy source. Energy demand increases with population growth, making the search for other resources for energy generation necessary. Since the Industrial Revolution, coal became the dominant energy generation resource, followed with the discovery of oil and gas over the following decades¹. Until today, these three resources (which are generally called fossil fuels) dominate the energy generation industry due to their inherent energy-superior properties related to efficiency, convenience and logistics².

Fossil fuel reserves were formed over millions of years as the organic materials were decomposed and compressed into dense deposits of carbon-based reservoirs of condensed energy. Due to this reason, fossil fuels are incredibly energy-dense; with values of 24 MJ/kg for coal, 44 MJ/kg for crude oil, and 55 MJ/kg for natural gas³, making them among the most efficient energy generating resources. Besides that, fossil fuels are also ready-made since the production of the resources has already been done by mother nature millions of years ago. In addition, fossil fuels nowadays require little to no effort as compared to other energy resources, in terms of developing efficient energy collection, generation, conversion, and storage. This ability to generate energy on demand, however, wherever, and whenever, results in the high conveniency of fossil fuels, where other resources currently lack in one or more aspects. Furthermore, due to the extensive development of fossil fuel technologies since the commercial use of steam engines during the Industrial Revolution⁴, society advanced in various aspects such as living, working and traveling, relying more on technological inventions centred around them⁵. This well-established technological development that is dependent and intertwined with the energy generated from fossil fuels gave rise to advanced logistic supports, enabling seamless integration into society.

However, fossil fuels are non-renewable energy resources. Statistics estimated the availability of fossil fuel resources based on reserves to production (R/P) ratio to be ~132 more years for coal and ~50 more years for oil and gas⁶. However, these estimates are only a static measure which may vary depending on the capacity to economically source and extract fossil fuels, along with levels of

consumption. Thus, depletion of fossil fuel reserves could become a pressing issue over the years.

Besides that, prolonged use of fossil fuels for energy generation poses some serious issues concerning human safety and health and the environment. Processes related to the procurement of fossil fuels including mining, fracking, and refinery require huge manpower that involve works with high-risk of fatal accidents. An estimate suggests the number of fatalities related to coal mining is $\sim 12,000$ people a year⁷, while oil and gas related fatalities in the United States alone reach a statistic of ~28 deaths per 100,000 workers8. In addition, the extraction of fossil fuels also brings harm directly to the environment, such as local habitat destruction and fragmentation, visual and noise disturbance, gas and oil transportation pollution, water contamination, and spills in marine environments^{9,10}, or indirectly through facilitating other threats such as deforestation driven by road construction, human expansion into previously wild areas, the introduction of invasive species and pathogens, soil erosion, water pollution, and illegal hunting⁹. To put a number on how severe one of the environmental impacts of fossil fuel extraction is, the International Tankers Owners Pollution Federation estimates that between 1970 and 2016, spillages of oil totalled 5.73 million tons¹¹.

Furthermore, the use of fossil fuels for energy generation also harms human health and the environment. The burning of fossil fuels releases harmful by-products such as carbon dioxide in general, mercury and sulphur dioxide from coal burning, and carbon monoxide and nitrogen oxide from oil and gas burning¹². These emissions lead to serious environmental effects like, accumulation of greenhouse gases, acid rain, and toxic smog13, which will cascade into possible catastrophes towards human health and the environment such as global warming, ocean acidification, and respiratory damage in humans, if left unchecked. From the listed pros and cons, it is obvious that the disadvantages outweigh the advantages in the long run. Thus, the need for alternative resources for energy generation industries to produce energy in a much cleaner and sustainable way, should be of utmost importance. However, switching to other energy resources would mean rethinking the way society functions and understands energy and everything that revolves around it, which needs continuous and expansive efforts.

At the beginning of the 20th century, hydropower was added to the energy mix, followed by nuclear energy in the 1960s. Later in the 1980s, modern renewables such as solar and wind energy were also introduced¹. Even though new and renewable energy resources have been unlocked, energy consumption also increased, which outbalances the energy mix making the use of fossil fuel for energy generation still prominent. Annual global energy consumption has been increasing steadily over the past decades up to >160,000 TWh in 2019, with only $\sim 11\%$ of the energy generated coming from renewable resources¹⁴. One of the main reasons for the lack of renewable energy resources' integration into the energy mix is due to the current technical limitations of renewable energy technology¹⁵. Power generation from renewable resources depends on natural resources that are uncontrollable by humans. For example, solar energy is generated only during daytime, while wind energy depends on the wind speed; if it is very low, the turbine will not turn or if it is too strong it can damage the generator, and therefore a delicate balance needs to be maintained in order to keep a consistent generation of energy¹⁶. This inconsistent energy production leads to complex problems in integrating renewable energy technologies into the energy mix.

Besides that, good power qualities is needed to ensure stable and efficient supply to the grid¹⁷. A good power quality allows the system to work with high reliability and low costs, which is important in critical cases where blackout or noise can be a serious problem, such as in hospitals or computer centres¹⁸. Conversely, poor power qualities including voltage sags, swells, and flickers, voltage imbalances and variations, voltage-current harmonics, and interruptions will lead to higher possibility of equipment failures and high operating costs¹⁹. Thus, for a renewable energy system to be connected to the grid, a good power quality is essential, which requires complex additions to the system such as transformers, regulators, converters, and capacitors. The complexity providing good power quality of renewable energy to the grid increases the installation and maintenance cost, making it harder for renewable energy to be integrated into the energy mix.

Furthermore, most renewable energy resources require large areas of space to produce enough energy to be connected to the grid, due to low power density²⁰, making the technology dictated by location, which can be placed where it is hardly accessible to consumers. This in turn will increase the distance between renewable energy supplies and the grid, significantly affects the cost and efficiency due to transmission power loss²¹. Due to the mentioned geographical constraints, weather and climate will be another important variable to be put into consideration in determining the appropriate plant location, adding complexity in the integration of renewable energy technologies into the energy mix. On the other hand, if the technology is possible to be integrated into public construction such as rooftop solar panels, aesthetic impacts towards public perception will be another challenge for the integration of renewable energy technology into the energy mix.

Nowadays, the search for cleaner and more sustainable (renewable) energy resources has become a global mainstream topic among researchers. Solar cells and thermoelectric generators (TEGs) are among the renewable energy harvesting technologies that are currently being researched in vast. A solar or photovoltaic (PV), cell is a device that converts light energy into electrical energy through the photovoltaic effect²². The photovoltaic effect was first discovered by a French physicist Edmond Becquerel when he experimented with a solid electrode in an electrolyte solution and observed a voltage developed when the light fell upon the electrode²³. Several decades later, a working solar cell was invented by Charles Fritts in 1883 using selenium (Se) semiconductor and gold (Au) junction²⁴. In 1940, another breakthrough in solar cell technology occurred with the discovery of pn junctions by Russel Ohl when he investigated some silicon samples, one of which had a crack in the middle, where he noticed that current flowed through when it was exposed to light²⁵. This crack marked the boundary between regions containing different levels of impurities, making one side positively doped and the other negatively doped. Therefore, a positive charge builds up on one side and a negative charge on the other side of the p-n barrier, creating an electric field. He then developed the first p-n junction silicon solar cell in 1941, which he patented in 1946²⁶. However, the efficiency of solar cells at that time was incredibly low ($\sim 1\%$) until silicon solar cell capable of 6% energy conversion efficiency was fabricated by Gerald Pearson, Daryl Chapin, and Calvin Fuller in 1954²⁷.

In order to achieve global commercialization, different concepts, such as concentrator^{28–30} and multijunction^{31–33} solar cells, assorted materials such as polycrystalline silicon^{34–36}, perovskites^{37–39}, and organic polymers^{40–42}, and various architectures such as thin film^{43–45} and tandem^{46–49} solar cells, have been studied in solar cell research to

improve the efficiency and robustness while optimizing cost. Solar cell technologies have progressed so much nowadays that their energy conversion efficiencies have reached up to ~47%⁵⁰. Due to the vast area of research related to solar cells, they have been classified into three categories or generations based on its technology used; the first generation solar cells were comprised of photovoltaic technology based on thick silicon crystalline films^{51,52}, second generation solar cells were based on thin film technology applying the use of polycrystalline silicon and other semiconducting materials⁵³ such as copper indium gallium sulphide (CIGS)^{54,55}, cadmium telluride (CdTe)^{56,57}, and copper zinc tin sulphide (CZTS)^{43,58}, and third generation solar cells were fabricated using technologies focused on charge and energy transfer processes, and routes to optimize charge collection and enhance the energy harvest within the solar spectrum⁵⁹.

Perovskite solar cell (PSC) is one of the third generation solar cells that was recently developed, with promising performance improvement over the years. To put it into perspective, the conversion efficiency of PSCs has improved around 500% in less than five years as compared to second generation thin film solar cells based on chalcogenide materials, which took 35 years to achieve similar improvements⁶⁰. Currently, all-solid-state PSCs may achieve up to 25.2% power conversion efficiency⁶¹, with proper materials and fabrication. Device architecture of PSCs was initially developed based on the solid-state mesoporous architecture of dye-sensitized solar cells⁶², with an optimization of architecture leading to the current commonly used planar heterojunction architectures either as shown in Figure I.1. However, PSC suffers from poor device stability intrinsically due to molecular dissociation and ion migration, or extrinsically from decomposition and phase segregation due to exposure towards moisture, oxygen, light and heat⁶³.



Figure I.1: Planar heterojunction architectures of PSC.

Electron and hole transport layers play an important role in improving the efficiency and stability of PSCs⁶⁴, making the selection of suitable materials crucial. A suitable transport layer material should have a good stability toward the perovskite, low cost, good solubility and film forming properties for a full layer coverage to prevent current leakage, and high transmittance level if to be put facing the sunlight⁶⁵. For the hole transport layer (HTL), additional properties include high hole mobility, compatible highest occupied molecular orbital (HOMO) energy level with perovskite, and efficient electron-blocking property⁶⁰. Conversely, a good electron transport layer (ETL) should have high electron mobility, compatible lowest unoccupied molecular orbital (LUMO) energy level with perovskite, and efficient hole-blocking property⁶⁶.

As of now, the commonly used transport layer materials for PSCs are organics due to their superior performance and easier application. However, inorganic transport layers provide better stability^{67–70} thus efforts have been made to improve inorganic transport layers in terms of efficiency and ease of fabrication. Recently, inorganic ETLs seemed to have caught up with their organic counterpart, while inorganic HTLs are still lagging behind organic HTLs⁶⁵. Thus, the search for a suitable inorganic hole transport material to improve performance and stability is crucial for the commercialization of PSC technology.

TEG is a solid-state device that can convert heat into electricity, and vice versa, through the Seebeck, Peltier, or Thomson effects⁷¹. The Seebeck effect was coined after the German physicist Thomas Johann Seebeck, when in 1821 he discovered that an electromagnetic field developed when two strips of different electrically conducting materials joined together at their ends were subjected to a temperature difference^{72,73}. Then, came along Peltier effect in 1834 when the French physicist Jean Charles Athanase Peltier discovered that heat generated from a setup similar to Seebeck's is not consistent with the prediction from ohmic heating caused by electrical resistance⁷⁴.

However, Seebeck and Peltier failed to describe their discovery of the phenomena until William Thomson, later known as Lord Kelvin, drew the connection between both phenomena and contributed to the understanding of thermoelectricity. In 1851, he communicated his theoretical considerations based on his observation regarding the law of thermoelectric as we know today, stating that in an unequally heated circuit of two metals, an electric current must exercise a convective effect on heat, where different parts are kept at different temperatures⁷⁵. This in turn gave rise to the Thomson effect, where the heat absorbed or evolved along the length of a material whose ends are at different temperatures is proportional to the flow of current and to the temperature gradient along the material⁷⁶.

TEGs have attractive features for renewable energy applications including long life, no moving parts, no emissions of toxic gases, low maintenance, and high reliability⁷⁷. In the beginning, TEGs were used for energy generation in niche applications such as deep space exploration⁷⁸ and no-crew remote facilities⁷⁹. Nowadays, they have been used in a wider scope of energy generation such as waste heat recovery^{77,80} and several other applications including, semiconductor cooling, and temperature sensors⁸¹. **Figure I.2** shows the basic architecture of a TEG along with its energy generation mechanism.





Even though the development of TEG technologies vastly improved in the past decades, public commercialization still poses a problem, mainly due to the high cost of preparing high performing generators, which are dominantly based on expensive and rare materials such as tellurium (Te) and bismuth (Bi), along with complex preparation methods⁸². Thus, the fabrication of a low-cost TEG with good performance may push the development of this technology towards commercialization.

CZTS is a semiconducting material belonging to the quaternary chalcogenide group, consisting of copper (Cu), zinc (Zn), tin (Sn) cations and sulfur (S) as anion, with formula of (I)₂(II)(III)(IV)₄, respectively. Depending on the arrangement of its cations, CZTS can be found in several different crystal structures including cubic, hexagonal, and tetragonal⁸³. However, the most stable crystal structure is kesterite-CZTS with I-4 space group⁸⁴, as shown in Figure I.3. Besides that, CZTS possesses intrinsic p-type conductivity due to the presence of Cu_{Zn} antisites that have low formation energy and deep acceptor level⁸⁵. The carrier concentration and mobility of CZTS are generally around ~1017 cm-3 and ~0.5-2.0 cm²/V·s^{86,87}. In addition, CZTS exhibits good visible light-harvesting properties due to its band gap energy of $\sim 1.5-1.6 \text{ eV}^{88,89}$, with conduction and valence bands around -3.8 and -5.2 eV, respectively^{90,91}. Moreover, CZTS is also able to withstand a temperature up to ~800 °C without being degraded, showing excellent thermal stability⁹².



Figure I.3: Unit cell for kesterite-CZTS crystal structure.

Due to the mentioned properties, CZTS was initially studied as a suitable light-absorbing material to replace copper indium gallium selenide (CIGS) in thin film solar cells⁶⁵, in pursuit of using a greener

and more sustainable material for renewable energy harvesting. In addition, CZTS also provides versatility in its system including cation arrangement^{93,94}, elemental composition^{95,96}, doping^{97,98}, and element substitutions^{99,100}, to alter its properties for specific applications such as absorption¹⁰¹ sub-visible wavelength and crystal structure improvement¹⁰² in solar cell. The highest efficiency achieved from CZTS-based thin film solar cells since its first study in 1997¹⁰³ is currently 12.6%⁴⁴, though the theoretical efficiency based on Shockley-Quiesser limit predicted to be $32.4\%^{104}$. This is due to various non-ideal recombination paths that were manifested by activation energies that are smaller than the band gap¹⁰⁵. Due to the slow progress in solar cell applications, research on CZTS has branched out towards other applications such as transport layer in PSC¹⁰⁶⁻¹⁰⁸, photocathodes in photoelectrochemical water splitting^{109–111}, p-type material in thermoelectric applications ^{112–115}, improvement on photodetectors ^{116–} ¹¹⁸, and chemical sensors^{119–122}.

In this thesis, the exploration of CZTS in alternative applications involving transport layer and thermoelectricity, as compared to the commonly researched thin film solar cell absorber layer, will be presented. This doctoral work was done to explore other prospects of a well-studied material, CZTS, benefitting of its known properties for other applications in energy harvesting. Studies done in this work involve understanding the properties of CZTS upon synthesis and fabrication, along with possibilities of fine tuning for better control throughout the process. Besides that, possible applications of CZTS in transport layer and thermoelectricity will be discussed, with further exploration on thermoelectricity involving the fabrication of a working device, along with performance studies.

This doctoral work was done with the aim to systemically investigate the prospect of alternative applications for CZTS in energy harvesting. The first stage of this doctoral work will emphasize the understanding of processes related to the synthesis and fabrication of CZTS, as well as their effects on material's properties. The following phase will involve an in-depth discussion on CZTS to be used as a transport layer in PSCs and its effect on device stability and performance. From the knowledge and information obtained from the first two stages, the last stage of this doctoral work will discuss the possibility of CZTS in thermoelectric applications, along with thermoelectric analyses of the fabricated CZTS. The work done in this stage was taken further with the fabrication and preliminary performance studies of a TEG using CZTS as p-type material. The author hopes that this thesis will provide a deeper understanding of CZTS and its vast possibilities in energy harvesting applications, not limited to be an absorber layer for thin film solar cells.

In the first chapter, a discussion of CZTS on its properties upon synthesis and fabrication was presented. CZTS nanoparticles ink was synthesized via the bottom-up approach of hot-injection method using metal chloride precursors, sulphur, and oleylamine as a ligand. CZTS thin films were then fabricated via spin coating of the synthesized ink, followed by thermal treatment. The effects of the fabrication parameters, such as ink concentration, spinning rate, and thermal treatment temperatures on the morphology and structural, optical, and electrical properties of the film were studied, showing the possibility of controlling CZTS thin film properties by manipulating the fabrication parameters. It was found that ink concentration and spin-coating speed can be used to manipulate the film thickness, thus in turn affecting the film's optical properties. Moreover, it was found that thermal treatments significantly affect the film properties in terms of phase formation and crystallinity, as well as the electrical conductivity.

For the second chapter, a short review presented the progress in the studies of an alternative hole transport material for PSC, CZTS. Power conversion efficiency of PSCs has significantly improved in recent years, with the current highest recorded efficiency of 25.2%. One of the significant components of PSCs that contributed to this improvement is the transport layer, necessary in the separation and injection of charge carriers. Over the years, organic HTLs such as 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-

spirobifluorene (spiro-OMeTAD) have been investigated, developed, and utilized successfully. However, facile and low-cost synthesis, good stability, yet efficient HTL remains to be a major challenge. Therefore, alternative HTLs based on inorganic materials are being studied. CZTS is known for its ease of synthesis and band tuning, composition based on abundant and non-toxic elements, good electrical properties, and superior stability. Due to its good inherent properties, it is no wonder why CZTS is being researched to be used as a HTL. This chapter will focus on the integration effects of CZTS as a HTL in PSCs, along with possible opportunities for further improvement. The third chapter discussed the use of CZTS thin film for thermoelectric applications, in terms of fabrication, material properties and preliminary performance analysis. CZTS thin films were fabricated applying the knowledge obtained in chapter one, with the addition of thermoelectric transport property analyses of the fabricated films. Due to its abundance of elements and non-toxicity, CZTS is considered as a sustainable "green" material and will be used as a p-leg to be coupled with an n-leg of aluminium-doped zinc oxide (AZO) in a TEG, to demonstrate the feasibility of using this material in the thermoelectric technology. In addition, preliminary performance analyses of the fabricated TEG will be discussed, along with plans for further improvement and optimization.

Finally, as concluding remarks, the author's perspective, prospects, and ongoing works, regarding this doctoral work are presented. Even though the performed studies are currently focused on re-exploring the properties of CZTS to suggest an alternative use in energy harvesting, possibilities for promising future research stemming from this work are limitless, including but not limited to dimensional reduction and its effects on properties, material modifications, and device improvement. Besides that, the efforts done in this thesis may also reinvent the way researchers look at widely studied materials, to search for alternative applications which may still be of benefit.

1. Solution-based synthesis and characterization of Cu₂ZnSnS₄ (CZTS) thin films

Published under a CC BY 4.0 license.

This section is entirely taken from¹²³: Solution-based synthesis and characterization of Cu_2ZnSnS_4 (CZTS) thin films. Ubaidah Syafiq, Narges Ataollahi, Rosa DiMaggio, and Paolo Scardi. *Molecules*. 2019. 24 (19). DOI: 10.3390/molecules24193454

Please cite any part of this section as specified above.

Ubaidah Syafiq ^{a,b}, Narges Ataollahi ^a, Rosa Di Maggio^a and Paolo Scardi^{a,*}

^a Department of Civil, Environmental and Mechanical Engineering, University of Trento, Via Mesiano, 77, 38123 Trento, Italy; muhammad.mustaffa@unitn.it (U.S.); narges.ataollahi@unitn.it (N.A.); rosa.dimaggio@unitn.it (R.D.M.)

^b Solar Energy Research Institute, National University of Malaysia (SERI-UKM), Bangi 43600, Selangor, Malaysia

* Correspondence: paolo.scardi@unitn.it; Tel.: +39-0461282417; Fax: +39-0461281999

Abstract

Cu₂ZnSnS₄ (CZTS) ink was synthesized from metal chloride precursors, sulphur, and oleylamine (OLA), as a ligand by a simple and low-cost hot-injection method. Thin films of CZTS were then prepared by spin coating, followed by thermal annealing. The effects of the fabrication parameters, such as ink concentration, spinning rate, and thermal treatment temperatures on the morphology and structural, optical, and electrical properties of the films were investigated. As expected, very thin films, for which the level of transmittance and bandgap values increase, can be obtained either by reducing the concentration of the inks or by increasing the rate of spinning. Moreover, the thermal treatment affects the phase formation and crystallinity of the film, as well as the electrical conductivity, which decreases at a higher temperature. **Keywords**: Cu₂ZnSnS₄; thin film; spin coating; morphology; optical properties; phase change; electrical properties

1.1. Introduction

Kesterite, or CZTS, is a quaternary sulphide containing copper (Cu), zinc (Zn), tin (Sn), and sulphur (S) with the formula $(I)_2(II)(III)(IV)_4$. As a semiconducting compound, kesterite has p-type conductivity¹²⁴ and can withstand temperature up to 800 °C⁹². It was initially considered as an adsorbing material in thin-film solar cells to replace Cu(In,Ga)Se₂ (CIGS), whose elements are expensive and scarcely available. Indeed, CZTS exhibits good light-harvesting performance, with an optimal band gap energy around 1.5-1.6 eV^{88,89}, given by conduction and valence bands around -3.8 and -5.2 eV, respectively^{90,91}. The external quantum efficiency (EQE) for CZTS solar cells shows that the light-harvesting process starts from about 400 nm up to more than 800 nm¹²⁵ radiation wavelength.

Nowadays, the fabrication of films from CZTS suspension through the ink-based approach has attracted considerable research interest as a simple, economic, and industrially scalable route, compared to the more expensive vacuum deposition methods. This method allows better material utilization with high throughput. Moreover, an ink-based approach lets simple deposition methods, such as spin coating, dip coating, spray coating, screen printing and ink-jet printing, be used¹²⁶⁻¹²⁸. Inks were prepared by solvo-thermal methodology, one of the simplest and fastest ways to synthesize highquality CZTS nanoparticles on the gram scale, which involves the injection of a sulphur solution into a hot mixture of metal precursors dissolved in a solvent with a high boiling point¹²⁹. In this regard, and despite the progresses in the production process, fine control of the composition, shape, and size of CZTS nanoparticles requires complex metal sources, solvents, and ligands. Several studies demonstrated that solvents can affect the final shape of CZTS nanoparticles^{130,131}, whereas the sulphur source and reaction temperature can affect the crystal structure¹³². Actually, a simple approach based on metal chlorides, sulphur powder and oleylamine (OLA), playing a double role of solvent and complexing agent, has been already proposed^{89,133} to produce quaternary CZTS nanoparticles on the gram scale. A similar method has been successfully employed for producing CZTS nanoparticles for solar cell applications, with a device efficiency up to $10.3 \ \%^{134}$.

Where the electrical properties of binary and ternary semiconductors have been studied for years^{135–137}, those of CZTS have been investigated more recently^{138,139}, especially taking into account their temperature dependence. In general, the electrical conductivity of CZTS films is due to Mott variable-range hopping and nearest neighbour hopping mechanisms below -125 °C. Above that temperature, the conductivity increases because of either thermionic emission of carriers over grain boundary barriers or the release of carriers from defect states¹⁴⁰. In summary, two distinct modes of electronic transport are observed: hopping conduction (less than -125 °C) and thermally activated conductivity (greater than -125 °C). For ink-based CZTS thin films, it is reported that an increase in thermal treatment (TT) temperature increases the conductivity of the film, but evidence on this important aspect of the production process is still limited¹³⁹.

So far, properties of micrometric and sub-micrometric (>0.5 µm) CZTS thin films fabricated using several different methods have been extensively studied^{58,125,141-143} with the purpose of being the absorber layer in solar cell. There are also studies on CZTS thin films with $<0.5 \mu m$ thickness, in which they are used as a transport layer in a PSC^{106–108}. However, their focus is on the application of the thin film in the solar cell, with limited information on properties. Thus, this study focuses on the influence of deposition parameters and thermal treatment on the morphology and structural, optical, and electrical properties of CZTS thin film synthesized using a hot-injection method, which has not, to the best of our knowledge, been reported in the literature. The main novelty of this study is the effect of thermal treatment on the crystal structure, which further affects other properties of the films at $<0.5 \mu m$ thickness. The results of this study can provide some insights on the versatility of CZTS, not just as a traditional absorber layer, but as transport layer.

1.2. Results and discussion

1.2.1. CZTS ink concentration and spin rate The first parameter studied was ink concentration. **Figure 1.1a,b** shows the images from optical microscopy of the CZTS thin film with 0.5 and 0.2 g/ml of CZTS nanoparticles in toluene, respectively; the lower the concentration, the lower the number of surface irregularities. The increase of CZTS nanoparticles per unit volume increased the possibility of agglomeration, which reduced the surface energy^{144,145}. On the contrary, CZTS nanoparticles were better dispersed in a more diluted solution, thus providing a smooth and continuous layer of CZTS.



Figure 1.1: Surface of the Cu₂ZnSnS₄ (CZTS) thin film: (**a**,**b**) optical microscopy and (**c**,**d**) scanning electron microscopy (SEM) prepared by using ink with concentrations of nanoparticles at 0.5 and 0.2 g/ml, respectively.

Figure 1.1c,d shows the corresponding SEM pictures of the surface morphology of CZTS thin films with different ink concentrations deposited on fluorinated tin oxide (FTO) glass. In general, the obtained thin films consisted of continuous layers of CZTS nanoparticles that homogenously covered the entire surface of FTO glass. However, some agglomeration, highlighted by red circles, was visible on CZTS thin films prepared with 0.5 g/ml ink. After deposition, the higher packing density forced some nanoparticles to form agglomerates, resulting in a lower surface energy¹⁴⁶.

SEM observations of the cross-section of the thin films with different ink concentrations (Figure 1.2) allowed us to evaluate the

thickness of the thin films. The average thickness observed for CZTS thin films with 0.5 and 0.2 g/ml concentrations were \sim 336 and \sim 135 nm, respectively. As expected, the higher the ink concentration, the thicker the thin films were.



Figure 1.2: Cross-section of the CZTS thin film on fluorinated tin oxide (FTO) glass by SEM, prepared with ink having concentrations of (**a**) 0.5 g/ml and (**b**) 0.2 g/ml, respectively.

Figure 1.3a shows the ultraviolet-visible (UV-vis) spectroscopy results with different ink concentrations. The CZTS thin film with 0.2 g/ml ink has a higher transmittance level compared to 0.5 g/ml ink. UV-vis spectroscopy (**Figure 1.3b**) of the CZTS thin film deposited on the FTO glass shows that with an increasing spin rate, the transmittance correspondingly increases. According to Beer–Lambert's law, a decrease in thickness of a material will decrease its absorption, thus causing an increase in transmittance^{147,148}. This result confirms that the lower the ink concentration and the higher the spin rate are, the thinner the CZTS film will be.

Tauc's plot of CZTS thin films with different ink concentrations are shown in the insert of **Figure 1.3a**. The band gaps for CZTS thin films were \sim 1.45 and \sim 1.68 eV, for inks having nanoparticle concentrations of 0.5 and 0.2 g/ml, respectively.

Although the band gaps obtained were still in accordance with the band gap range of CZTS reported in the literature^{88,90,91}, the decrease in band gap with an increasing concentration can be related to the greater thickness of CZTS thin film deposited. There is a possibility of structural defects in the film, which could give rise to localized states near the conduction band. In the case of thick films, these localized states may as well merge with the conduction band, resulting in a reduction of the bandgap¹⁴⁹.



Figure 1.3: UV–vis spectroscopy of the CZTS thin film (a) prepared by ink having concentrations of 0.5 g/ml (red line) and 0.2 g/ml (black line), the insert is Tauc's plot of corresponding CZTS thin film, and (b) at different spin rates: black line, 2000 rpm; red line, 4000 rpm; and blue line, 6000 rpm.

1.2.2. TT temperature

The effect of TT temperature on CZTS thin film samples, obtained from 0.2 g/ml ink spread at a 6000 rpm spin rate, was studied in terms of its surface morphology, grain growth, optical behavior, and electrical properties. **Figure 1.4** shows the micrograph of the surface of CZTS thin films treated at temperatures from 150 to 350 °C. The treatments in the range 240-280 °C seemed to induce cracks in samples, probably because of excessive drying and the shrinkage rate^{150,151}. In fact, the samples treated at 150 and 200 °C appeared smooth and continuous. Also, the thin films treated at 300, 320, and 350 °C did not show cracks because, at those temperatures, the CZTS grain growth¹⁵² and phase changes compensated the shrinkage and avoided crack formation.



Figure 1.4: Morphology of the CZTS thin film surface by optical microscope at different TT temperatures indicated on each micrograph.

In **Figure 1.5**, the X-ray diffraction (XRD) spectra of the samples treated at 200, 350, and 500 °C are shown, demonstrating that different CZTS phases formed. At TT 200 °C, a mix of cubic (distinctive peaks at $2\theta = \sim 33.2^{\circ}$, $\sim 38.5^{\circ}$, $\sim 55.7^{\circ}$, and $\sim 66.3^{\circ}$) and hexagonal, also known as wurtzite (at $2\theta = \sim 31.4^{\circ}$, $\sim 35.3^{\circ}$), CZTS phases formed¹⁵³. At TT 350 °C, only cubic CZTS phase formed¹⁵⁴. At TT 500 °C, a tetragonal (distinctive peaks at $2\theta = \sim 18.9^{\circ}$, $\sim 21.3^{\circ}$, and $\sim 38.5^{\circ}$)^{133,155} peak formed, and also a secondary phase, tin (II) sulphide (SnS), formed having main peaks at $2\theta = \sim 25.8^{\circ}$, $\sim 30.4^{\circ}$, $\sim 31.9^{\circ}$, $\sim 35.6^{\circ}$, $\sim 36.8^{\circ}$, $\sim 37.2^{\circ}$, and $\sim 45.7^{\circ}$. It was demonstrated¹⁵⁴ that when the nanocrystals of CZTS are very small, they can be cubic or hexagonal, and with increasing size, one observes cubic only, which evolve to the thermodynamically stable tetragonal form when crystals are big enough.

The crystallization process, and especially the grain growth, as demonstrated by the sharpness of peaks, was strongly promoted at 500 °C, while the formation of a secondary phase (SnS) might be due to unbalanced stoichiometry¹⁵⁶.



Figure 1.5: XRD spectra of CZTS thin films treated at 200 °C (black line), 350 °C (red line), and 500 °C (blue line). Identified phases are indicated by corresponding symbols.

The Williamson–Hall (W-H) analysis^{157,158} was performed on XRD data to study the effect of the TT temperature on the size of the nanocrystals and on the microstrain. The latter was due to the surface of the nanocrystals but can also be caused by stoichiometric fluctuations¹⁵⁹. As shown in **Figure 1.6**, the microstrains at TT 200 °C and TT 350 °C are greater than that at TT 500 °C. The reduction of the microstrain is probably related to the consequent increase in the size of the crystals, since OLA, which acts as the ligand, is decomposed at TT 500 °C, resulting in further grain growth.



Figure 1.6: The Williamson–Hall (W-H) analysis (β, integral breadth of diffraction peaks; θ, Bragg diffraction angle) of CZTS thin films treated at 200 °C (black line), 350 °C (red line), and 500 °C (blue line).

Figure 1.7 shows the UV-vis spectroscopy of CZTS thin films deposited on FTO glass under three different TTs. The shift of the transmittance curve towards the visible range for the film treated at 350 °C compared to 200 °C was due to the absence of a wurtzite phase. As reported⁹⁴, films containing wurtzite phase show higher absorptions in the visible range. Furthermore, the transmittance of the film treated at 500 °C showed a shift toward higher wavelengths due to Sn loss¹⁶⁰. The maximum peak of transmittance for TT 200 °C and TT 350 °C was ~65%; however, it was reduced to ~55% for TT 500 °C. This was due to grain growth, which leads to an increase in surface roughness, causing increased scattering and absorption of light¹⁶¹.



Figure 1.7: UV–vis spectroscopy of CZTS thin films at different TT temperatures: black line, 200 °C; red line, 350 °C; and blue line, 500 °C.

From the UV-vis spectroscopy data, the band gaps of the thin films were determined to be at ~1.62 eV for TT 200 °C, ~1.57 eV for TT 350 °C, and ~1.73 eV for TT 500 °C, respectively, which is in good agreement with those reported in the CZTS literature ^{88,90,91}. However, the slight differences observed among the samples might be due to the different phases present in each sample. In fact, samples at TT 200 °C and TT 350 °C showed a similar band gap because a cubic CZTS phase was prevalent in both, although the wurtzite in the TT 200 °C sample favoured a shift of the band gap towards a higher value¹⁶². The presence of multiple and spurious phases favours the increase of the optical absorption edge towards higher energy values¹⁶³ and is confirmed by the high band gap value of the sample treated at 500 °C.

The electrical properties of CZTS thin films were studied at different TT temperatures (TT 200 °C, 350 °C, and 500 °C) by Hall effect measurements. Results shown in **Table 1.1** refer to CZTS thin films deposited on soda-lime glass (SLG) as FTO interfered with the measurement of such thin layers. The value of resistivity decreases significantly as the TT temperature increases to 500 °C, which is in agreement with literature^{164,165}. Phase changes and microstructures are known to play a role in the electrical properties of CZTS. The resistivity of tetragonal CZTS is lower than other CZTS phases⁸³, and grain growth and refining are promoted by high-temperature TTs, reducing

the amount of defects¹³⁹. However, the large difference observed in resistivity and carrier concentration most probably depends on the presence of organic residuals in the lower temperature TTs^{133} .

While resistivity and carrier concentration obtained at 500 °C were better than literature values^{95,166}, mobility was lower. It has been already observed that carrier mobility is strongly dependent on the microstructure and secondary phase¹⁶⁵, like SnS that formed at 500 °C. Since the carrier mobility is inversely proportional to the resistivity, eliminating the SnS secondary phase will increase carrier mobility, further reducing the resistivity and, thus, improving the overall electrical properties of the CZTS thin film.

 Table 1.1. Hall effect measurement results of CZTS thin films with different TT temperatures.

Sample	Thickness (nm)	Resistivity, ρ(Ω·cm)	Carrier concentration, n (cm ⁻³)	Carrier mobility, µ (cm²/Vs)
ТТ 200°С	~135	4.0x10 ⁴	2x10 ¹³	13
ТТ 350°С	~100	4.6x10 ⁴	5x10 ¹²	27
ТТ 500°С	~90	4.1x10 ⁻¹	$1x10^{21}$	0.5

The better electrical properties of the film made at 500 °C was also demonstrated by cyclic voltammetry (CV) measurements. The cathodic current density (J_{pc}) was determined by the difference between the maximum peak current density and the baseline of charging current density¹⁶⁷. It is worth noting that the peak at the negative potential corresponds to the reaction $I_3^- +2e^- \rightarrow 3I^-$, where the current density can be related to the rate of reduction of I_3^- to I⁻, occurring at the CZTS electrode. As shown in **Figure 1.8**, TT 500 °C had the highest current density, which can be explained by a better electrocatalytic ability of the electrode¹⁶⁸. In general, CV confirmed the Hall effect results, demonstrating the importance of high-temperature TTs to make CZTS thin films with better electrical properties. The question that still remains is how to avoid the formation of secondary phases, which are detrimental to the mobility of the carriers.



Figure 1.8: CV of CZTS thin films with different TT temperatures: black line, 200 °C; red line, 350 °C; and blue line, 500 °C.

1.3. Materials and methods

Copper (II) chloride dihydrate (CuCl₂·2H₂O, >99.0%), zinc chloride (ZnCl₂, >98.0%), and tin (II) chloride (SnCl₂, 98%) were purchased by Sigma-Aldrich Inc. and dehydrated in vacuum at 200 °C. Sulphur (S), oleylamine (OLA, 70%), toluene (99.9%), and ethanol (>99%) were also provided by Sigma-Aldrich Inc. and used without further purification.

1.3.1. Synthesis of CZTS nanoparticles ink

CZTS nanoparticles ink was prepared according to the method described by Ataollahi et al.¹³³: 0.538 g of CuCl₂·2H₂O, 0.414 g of ZnCl₂, and 0.410 g of SnCl₂ were mixed into a 100 ml three-neck roundbottom flask containing 6.6 ml of OLA. The system was connected to a Schlenk line apparatus to carry out the whole process in standard, airfree conditions. OLA was added to work both as a solvent and as a capping agent for the nanoparticles. The mixture was heated first to 130 °C, and at this temperature the flask was degassed and refilled with nitrogen several times and then kept under vacuum. About 8 ml of a sulphur/OLA 1 M solution (prepared by dissolving 0.449 g S in 10 ml OLA) was rapidly injected in the hot solution at 270 °C under fast stirring and nitrogen (N₂) flux. The mixture was kept at 270 °C for 30 min after the injection and then cooled slowly to room temperature. The obtained suspension of nanoparticles was washed with a mixture of 5 ml toluene and 25 ml ethanol and centrifuged for 10 min at 4000 rpm to separate the solvent from the nanoparticles. Finally, the CZTS nanoparticles were extracted, dispersed in toluene, and sonicated to obtain an ink with the desired concentration.

1.3.2. Deposition of CZTS thin film

The CZTS nanoparticles ink was deposited on SLG substrates by spin coating. Before deposition, the substrates were cleaned with soap, treated with concentrated potassium hydroxide (KOH) in ethanol, rinsed with distilled water and ethanol, then dried in N_2 stream. The cleaning process of the FTO glass was similar, except for the treatment with KOH, where 20 µL of ink was dropped on the substrate. After spin coating, the residual toluene was removed at 150 °C for 15 min. The TT below 350 °C was carried out on a hot-plate under N_2 atmosphere for 15 min. High-temperature TT (500 °C) was performed in a tubular furnace at a heating rate of 3 °C/min for 1 h under N_2 atmosphere. Samples were labelled according to ink concentration (0.2 and 0.5 g/ml), spin rate (2000-6000 rpm), and TT temperature (150-500°C).

1.3.3. CZTS thin film characterization

The morphology of CZTS thin film samples was observed either by optical microscopy or by scanning electron microscopy (SEM). Optical microscopy was made on a REMET HX-1000 (Remet, Bologna, Italy) at 400x magnification, whereas for SEM we used a JEOL JSM-7001F FEG-SEM (JEOL, Tokyo, Japan) equipped with an energy-dispersive X-ray spectroscopy detector (EDXS, Oxford INCA PentaFETx3, Oxford, United Kingdom). Observations were made at 10.00-15.00 keV electron beam energy with a working distance between 5-10 mm. Surface morphology images were acquired in top-down modes, whereas a cross-sectional analysis was performed by putting the cross-section of the film on a 90° stub.

UV-vis spectroscopy of CZTS thin films was made using a Perkin-Elmer LAMBDA 950 spectrophotometer (Perkin-Elmer, Milano, Italy) equipped with a 150 mm integrating sphere. By measuring normal incidence transmittance and reflectance, the absorption coefficient was calculated using the equation: Muhammad Ubaidah Syafiq bin Mustaffa – Alternative uses of CZTS thin films for energy harvesting

$$\alpha = -\frac{1}{d} \ln \left(\frac{T}{1-R} \right)$$

where;

 α = absorption coefficient,

d =film thickness,

T = normal incidence transmittance, and

R = normal incidence reflectance.

From UV-vis spectroscopy data, the bandgap energy was also obtained by a linear fit of a Tauc plot.

Structural information on CZTS thin films were obtained by Xray diffraction (XRD), using a Panalytical X'Pert MRD instrument equipped with CoK α sealed tube operated at 40 kV and 40 mA. Phase identification was supported by JADE Software (Materials Data, Inc., Livermore, CA, USA).

Hall effect measurements were made using an electrical testing platform (RH 2030 – PhysTech, Germany) with a current source range of 10^{-10} - 10^{-2} A, with maximum resolution of 2.5×10^{-12} A. The maximum output voltage was ± 20 V with the output resistance using a typical 10^{13} Ω resistor. Besides that, the voltage measurement range was 10^{-6} - 10^1 V, with maximum resolution of 3×10^{-7} V. The instrument had a sensitivity of <1 mV and an input resistance of $>10^{15}$ Ω . The magnetic field was provided by a standard magnet with magnetic field (B) range of 0.05-0.8 T and an achievable maximum resolution of 0.001 T. The pole diameter and gap were 45 and 0-75 mm, respectively. The resistivity value was calculated by using the formula:

$$\rho = \frac{1}{\sigma} = \frac{1}{q\mu n}$$

where;

 ρ = sample resistivity ($\Omega \cdot cm$),

 σ = sample conductivity ($\Omega^{-1} \cdot cm^{-1}$),

 $q = \text{charge constant (1.6x10^{-19} \text{ C})},$

 μ = carrier mobility (cm²/Vs), and

 $n = \text{carrier concentration (cm}^{-3}).$

Cyclic voltammetry (CV) was conducted on Princeton Applied Research (PAR) model no. 4000 A with a three-electrodes system. Silver/silver chloride (Ag/AgCl) was the reference electrode, platinum (Pt) was the counter electrode, and CZTS thin film samples were deposited on the FTO glass as working electrodes with iodide/triiodide ion (I^-/I_3^-) electrolytes using a methanol solution containing 0.5 M potassium iodide (KI) and 0.5 mM I₂. Scanning was done at a rate of 50 mV s⁻¹.

1.4. Conclusions

Ink containing CZTS nanoparticles was successfully synthesized by the hot-injection method using metal chloride precursors, sulphur, and OLA. It was found that the ink concentration affected the thickness and surface morphology of the deposited film. The spin rate can be manipulated to obtain films with different thicknesses. Both a lower ink concentration and a higher spin rate produced CZTS thin films with lower thickness, higher transmittance, and better morphology. Moreover, the different thermal treatment temperatures (from 150 to 500 °C) affect more than other parameters on the overall quality, surface morphology, crystal structure, transmittance behavior, band gap energy, and electrical properties of the CZTS thin film. The increase in TT temperature induces significant phase changes (wurtzite CZTS-cubic CZTS-tetragonal CZTS) in addition to an improvement in the crystallinity degree and electrical properties. While hightemperature TTs are required to get rid of organic residuals and increase conductivity and carrier concentration, they can also lead to the formation of secondary phases like SnS, which is detrimental to the mobility of the carriers. A correct balance between different requirements in thin film production still has yet to be found. The method is confirmed to be very versatile for preparing CZTS submicrometric thin films (< $0.5 \mu m$) and semiconductors suitable for a transport layer in many applications such as in solar cells, diodes, and thermoelectric devices.

Author Contributions: Conceptualization, P.S., N.A. and U.S.; methodology, U.S., N.A., and R.D.M.; experimental investigation, U.S. and N.A; resources, P.S. and R.D.M.; data curation and interpretation, U.S. and N.A; writing-original draft preparation, U.S.; writing-review and editing, N.A., P.S., and R.D.M.; supervision, P.S. and N.A; funding acquisition, P.S.

Funding: This research was funded by the Autonomous Province of Trento for the support provided within the framework of the programmatic Energy Action 2015–2017.

Acknowledgments: The authors thank Nicola Bazzanella for the SEM measurements, Puvaneswaran Chelvanathan for the Hall effect measurement, and Mirco D'Incau for the helpful comments and suggestions.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

2. Progress in CZTS as hole transport layer in perovskite solar cell

Published under a CC BY license.

This section is entirely taken from⁶⁵: Progress in CZTS as hole transport layer in perovskite solar cell. Ubaidah Syafiq, Narges Ataollahi, and Paolo Scardi. *Solar Energy*. 2020. 196, 399-408. DOI: 10.1016/j.solener.2019.12.016

Please cite any part of this section as specified above.

Ubaidah Syafiq^{a,b}, Narges Ataollahi^a, Paolo Scardi^{a,*}

^a Department of Civil, Environmental and Mechanical Engineering, University of Trento, Via Mesiano, 77, 38123 Trento, Italy

^b Solar Energy Research Institute, National University of Malaysia (SERI-UKM), Bangi 43600, Selangor, Malaysia

* Corresponding author. *E-mail address*: paolo.scardi@unitn.it (P. Scardi)

Abstract

Power conversion efficiency of perovskite solar cells (PSCs) has improved around 500% in less than five years, with the current highest recorded efficiency of a standalone PSC of 25.2%. One of the significant components of PSCs that contribute to this improvement is the transport layer, necessary in the separation and injection of charge carriers. Over the years, organic hole transport layers (HTLs) such as 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-

spirobifluorene (spiro-OMeTAD) have been investigated, developed, and utilized successfully, but facile and low-cost synthesis, good stability, yet efficient HTL remain to be major challenges. Therefore, alternative HTLs based on inorganic materials are being studied. This short review presents progress in the studies of an alternative HTL material for PSCs, Cu₂ZnSnS₄ (CZTS), known for the ease of synthesis and band tuning, composition based on abundant and non-toxic elements, good electrical properties, and superior stability. Focus is on the effects of integration of CZTS as HTL in PSC, and opportunities for further improvement. **Keywords**: Cu₂ZnSnS₄; Chalcogenide; Hole transport layer; Perovskite solar cell

2.1. Introduction

Global warming, energy production, and energy storage has become some of the popular discussion topics in society nowadays¹⁶⁹. To fulfil nowadays demands on energy; which must be achieved without increasing carbon dioxide (CO₂) emissions or relying on depleting fossil fuel resources, the development of advanced renewable energy technologies has become a global focus. Unlimited and clean solar energy is one of the main choices as a renewable energy source. The amount of energy that the Earth receives from the Sun is around $\approx 1.75 \times 10^{17}$ W, enough to fulfil the yearly energy world demand in less than an hour¹⁷⁰. Because of this, the development of photovoltaic technologies, or solar cells can be seen to emerge rapidly.

Nowadays, there are many types of solar cells being studied, applying assorted designs, concepts, and materials. In general, solar cells can be classified into three generations. The first generation solar cell technology comprised of photovoltaic technology based on thick silicon (Si) crystalline films¹⁷¹. Currently, first-generation crystalline silicon solar cell dominates the market. Even though silicon is widely available and inexpensive, the manufacturing of silicon in bulk is an energy-intensive process, thus leads to higher production costs¹⁷². Also, due to the indirect optical band gap, it requires a thick active layer for solar conversion¹⁷³. However, its high efficiency and good stability balance the disadvantages.

To reduce the fabrication cost, second generation solar cell is developed. It is based on thin film technology using amorphous silicon and other semiconducting materials such as copper indium gallium sulphide (CIGS), cadmium telluride (CdTe) and CZTS⁵³. CZTS is a semiconducting compound made of Copper (Cu), Zinc (Zn), Tin (Sn) and Sulphur (S); in the form of (I)₂(II)(III)(IV)₄. CZTS can exist in several different crystal structures such as cubic, hexagonal, and tetragonal⁸³, as shown in **Figure 2.1(a, b, c)**, respectively. Cubic (sphalerite) and hexagonal (wurtzite) crystal structures are metastable CZTS structures, that possess randomly distributed cations with different stacking order⁹². Given sufficient energy, CZTS will rearrange into a more stable, tetragonal crystal structure. Tetragonal CZTS can exists with several different polymorphs, depending on how the cations are arranged. Several known tetragonal CZTS polymorphs are stannite with I-42 m space group (S.G.), **Figure 2.1(d)**, CuAu-like (PMCA) with P-42 m S.G., **Figure 2.1 (e)**, and the most stable kesterite-CZTS with I-4 S.G.⁸⁴, **in Figure 2.1(c)**. In addition, kesterite-CZTS was also found to have different polymorphs depending on the Cu and Zn cations on the $z = \frac{1}{4}$ and $\frac{3}{4}$ planes. At elevated temperature (>260 °C), the aforementioned cations will be randomly distributed in the planes, leading to a second-order transition to disordered kesterite-CZTS with I-42 m S.G.¹⁵⁴, as shown in **Figure 2.1(f)**.



Figure 2.1: (a) Cubic-CZTS (S.G. F-43 m), (b) Hexagonal-CZTS (S.G. P63mc), (c) Ordered tetragonal kesterite-CZTS (S.G. I-4), (d) Tetragonal stannite-CZTS (S.G. I-42 m), (e) Tetragonal PMCA-CZTS (S.G. P-42 m), (f) Disordered tetragonal kesterite-CZTS (S.G. I-42 m).

Kesterite-CZTS was initially sought out as an active material to replace the expensive and scarce CIGS, in thin film solar cells. It exhibits good light-harvesting performance for solar cells, with an energy band gap around 1.5-1.6 eV^{89,133}. The respective conduction and

valence band values for kesterite-CZTS are -3.8 eV and -5.2 eV^{90,91}. In addition, band gap of CZTS can be tuned, along with further increment of absorption spectrum up to 1000 nm, made with the incorporation of selenium (Se) into the structure^{101,174}. CZTS, a p-type semiconductor¹²⁴, can withstand temperature up to 800 °C⁹². With proper fabrication technique, kesterite-CZTS solar cells may achieve up to 12.6% power conversion efficiency⁴⁴. External quantum efficiency (EQE) graph for kesterite-CZTS solar cells shows that light-harvesting process occurs in the range from 400 nm up to more than 800 nm^{125,175}. Even though the fabrication cost can be reduced, the performance of second generation solar cells is known to be still poor compared to the first generation¹⁷⁶.

Next, third generation solar cell is developed, aiming to overcome the high-cost and low efficiency solar cell problems. Significant attention was paid to charge and energy transfer processes, and routes to optimize charge collection and enhance the energy harvest within the solar spectrum⁵⁹. This generation of solar cell includes perovskites, quantum dots, and dye-sensitized solar cells (DSSCs). Third generation solar cells show great promise in their light harvesting mechanism. For example, PSCs show excellent light-harvesting properties,>50% in the spectrum range from 450 to 750 nm¹⁷⁷. In less than five years, the power conversion efficiency (PCE) of PSCs has improved around 500%, while thin film solar cells based on chalcogenide took 35 years to achieve similar improvement⁶⁰. This shows that perovskite materials have a promising future in solar cells technology. Perovskite materials are CaTiO₃-like crystal structure materials with ABX₃ formula, where A and B are two different cations, while X is an anion. The ideal cubic perovskite structure has Pm-3 m S.G. (Figure 2.2), with the arrangement of A cations in 12-fold cuboctahedra coordination and B cations in 6-fold coordination, surrounded by an octahedron of anions¹⁷⁸. However, since the relative ion size requirements are quite rigid, perovskite structures with lower symmetry and reduced number of cations coordination may arise due to buckling or distortion¹⁷⁹.


Figure 2.2: Cubic perovskite structure (S.G. Pm-3m).

Depending on the cations and anion used, perovskite materials option of exploitable properties such possess a wide as magnetoresistance, superconductivity, and electron-hole pair photogeneration¹⁸⁰. Perovskite materials such as CH₃NH₃PbI₃ proved to be a good absorber for solar cells. It has an energy band gap around 1.5 eV with conduction and valence band values of -3.9 eV and -5.4 eV, respectively^{181,182}. In addition, perovskite material can be modified for the purpose of energy gap tuning^{183,184}. It also has a long diffusion length¹⁸⁵, providing a more stable pathway for electron injection. Allsolid-state PSCs may achieve up to 25.2% power conversion efficiency⁵⁰, with proper materials and fabrication. EQE graph for perovskite materials shows that light-harvesting process occurs at spectrum around 400-800 nm^{186,187}.

Device architecture of PSCs is developing along with the needed criteria. In the beginning, a simple architecture of perovskite is introduced by incorporating the solid-state mesoporous architecture of dye-sensitized solar cells⁶². Later, improvement was made to the architecture with the aim of a simpler and cost-effective fabrication. It was found that perovskite can be used as its own layer for solar cells without any semiconducting scaffold¹⁸⁸. This led to the development of planar heterojunction PSCs, which is simple and cost-effective. The grain growth for planar heterojunction architecture is not limited to the

scaffold pore size, thus providing better charge-carrier mobility and slower recombination rate¹⁸⁹. Also, the simplicity of planar heterojunction architecture allows more creative ways of adopting and developing this technology for large-scale manufacturing⁶⁰. However, the PCE of planar heterojunction architecture is lower compared to the mesoporous architecture. This may be due to the slow electron injection rate from the perovskite material to the transport layer, compared to the solid-state mesoporous architecture¹⁸⁹. Still, the planar heterojunction architecture shows promising development; this in turn, leads to increasing study on optimization of the architecture.

In the beginning, the planar heterojunction architecture adopts the solid-state mesoporous architecture, in which n-type electron transporting material is deposited on a transparent conductive substrate, followed by the perovskite layer, p-type hole transporting layer, and top metal contact. This type of planar heterojunction architecture allows light to pass through the n-type electron transporting material first, before reaching the intrinsic perovskite layer. Due to this mechanism, this planar heterojunction architecture is called the n-i-p planar heterojunction architecture. However, the presence of large hysteresis can be observed in the current density-voltage (J-V) curve of this architecture¹⁹⁰; making the PCE measurement quite unreliable. Also, the diffusion length of holes is slightly shorter than electrons, due to a larger effective mass of holes¹⁹¹. This in turn, shifts the study towards the inverted (p-i-n) planar heterojunction architecture. In this architecture, the n-type electron transporting material is deposited on top of the perovskite layer. This enables the material to diffuse and react with the perovskite layer during processing, effectively stabilizing the electric properties, reducing the electric field-induced anion migration that may give rise to hysteresis, and thus resulting in no hysteresis¹⁹². Figure 2.3 shows a schematic of perovskite solar architecture evolution.



Figure 2.3: Evolution of PSC architecture⁶⁴.

Regarding efficiency, PSCs are developing to be almost as good as conventional, first-generation crystalline silicon solar cells. However, its stability for commercialization purpose is still questionable. The number of published studies on long-term device stability remains scarce⁶⁰. For PSCs to achieve commercialization, the stability should also be studied and improved. Transport layers play an important role in improving the efficiency and stability of PSC⁶⁴. Thus, the selection of suitable transport layers is crucial for PSCs. In general, a good transport layer should have good stability toward the perovskite, high transmittance level, if to be put facing the sunlight, and low cost. In addition, materials for HTLs should also have these properties: high hole mobility, compatible highest occupied molecular orbital (HOMO) energy level with perovskite for efficient hole transfer, and good solubility and film forming properties⁶⁰. As for now, the materials used as HTL can be categorized into organic polymers such as spiro-OMeTAD¹⁹³ and poly (3,4-ethylenedioxy-thiophene):poly(styrene sulphonate) (PEDOT:PSS)¹⁹⁴, and inorganic semiconductor materials such as metal oxides; nickel(II) oxide (NiO)¹⁹⁵ and copper(I) oxide $(Cu_2O)^{196}$, and metal chalcogenides; Cu_2BaSnS_4 (CBTS)¹⁹⁷.

Conversely, materials for ETLs should have high electron mobility, efficient hole-blocking property, and full layer coverage to prevent current leakage⁶⁶. Similarly, materials used for ETL nowadays can be categorized into organic polymers such as [6,6]-phenyl C61 butyric acid methyl ester (PCBM)¹⁹⁸ and amino-based polymers^{199,200}, and inorganic semiconductor materials such as metal oxides; titanium dioxide (TiO₂)²⁰¹ and zinc oxide (ZnO)²⁰², and metal chalcogenides;

zinc selenide (ZnSe)²⁰³. **Table 2.1** summarizes the categories and performances of several examples of materials used for transport layers in PSC. Even with poor stability, the performance of PSCs with organic transport layer is superior than the inorganic one, but the performance of inorganic ETL PSCs seem to have caught up with their organic counterpart, recently. However, inorganic HTL PSCs is still lagging on their performance as compared to organic HTL PSCs.

CZTS materials have been calculated to have theoretical solar cell efficiency of 32.4% based on Shockley-Queisser limit¹⁰⁴. However, the highest achievable efficiency up to now is lower than half (12.6%)⁴⁴, since its first study in 1997¹⁰³. Due to this unfortunate circumstance, research on CZTS has branched out towards other applications such as thermoelectric²⁰⁴ and transport layer¹²³, applying the already known knowledge and gaining new ones. Nowadays, it is well known that CZTS is an inorganic semiconducting material with good electrical properties, superior stability, facile and low-cost synthesis using nontoxic and abundant elements, and a tuneable band gap. Thus, it is no surprise that CZTS is currently being studied as an HTL in PSCs, especially when inorganic HTLs development is lagging behind their organic counterpart.

This paper presents a brief review on the progress in CZTS as HTL in rapidly developing, third generation, PSCs. This review is expected to give some insights on the studies done on CZTS, such as the method of synthesis, fabrication of film, and required properties for CZTS to be a good HTL. Besides that, this review might as well be a general guide for further studies on inorganic semiconductor materials as HTL, especially CZTS, on paving a new pathway towards the development of high-performance PSCs with superior stability, further directing them towards commercialization.

Transport layer	Category	Туре	Material	Architecture	PCE (%)	Researchers	Year published
	Organic	Polymer	Spiro-OMeTAD	n-i-p planar	16.9	Luo et al.	2019
	Organic	Polymer	PEDOT:PSS	p-i-n planar	18.0	Hu et al.	2018
	Inorganic	Metal oxide	NiO	p-i-n planar	planar 1.5 Tian et al.		2014
Hole	Inorganic	Metal oxide	Cu ₂ O p-i-n planar 11.0 Y		Yu et al.	2016	
	Inorganic	Metal chalcogenide	Cu2BaSnS4	p-i-n planar	10.1	Ge et al.	2017
Electron	Organic	Polymer	PCBM	p-i-n planar	20.6	Yang et al.	2019
	Organic	Polymer	Amino-based fulleropyrrolidine (C ₆₀ – N)	p-i-n planar	16.6	Li et al.	2016
	Organic	Polymer	Amino-functionalized copolymerp-i-n planar16.7Sun et al.		Sun et al.	2015	
	Inorganic	Metal oxide	TiO ₂	n-i-p planar	15.9	Wojciechowski et al.	2014
	Inorganic	Metal oxide	ZnO	n-i-p planar	20.7	Ma et al.	2019
	Inorganic	Metal chalcogenide	ZnSe	n-i-p planar	18.6	Li et al.	2018

Table 2.1: Example of materials used as transport layer in PSC.

2.2. Current progress on Cu2ZnSnS4 (CZTS) materials in perovskite solar cells

Due to its p-type conductivity, relevant conduction and valence band, band gap tuneability, and superior stability, research have been done to incorporate CZTS in PSC architecture. The following discussion is organized chronologically, starting with the first mentioned study in 2015 on the use of CZTS as HTL in PSC, until recent ones. Areas of discussion will include a brief description of the synthesis and deposition of CZTS, optical, structural, and electrical properties of the CZTS films, performance analysis of PSCs fabricated using CZTS as HTL, and effects of CZTS HTL on PSCs.

Wu et al.¹⁰⁶ reported the use of CZTS nanoparticles (NPs) synthesized from the hot injection method as HTL in an n-i-p perovskite (CH₃NH₃PbI₃) solar cell, as shown in Figure 2.4. The NPs were synthesized with varied reaction times, resulting in different particle sizes. The study showed that CZTS NPs with 20 ± 2 nm size with ~200 nm film thickness, yield the best efficiency when used as HTL in the solar cell. The reference PSC based on spiro-OMeTAD HTL showed an open-circuit voltage (Voc) of 1.07 V, a short-circuit current (Isc) of 18.94 mA cm-2, a fill factor (FF) of 65.0%, and a power conversion efficiency (PCE) of 13.23%; whereas PCE of PSC using the optimized CZTS HTL reached 12.75%; calculated from a V_{OC} of 1.06 V, an I_{SC} of 20.54 mA/cm², and a FF of 58.7%. The result showed that CZTS NPs HTL can transport holes as effectively as the widely-used HTL for PSC, spiro-OMeTAD. The decrease in FF for CZTS PSC is attributed to the increase in series resistance (R_s), suggesting an increase in leakage current due to the lower coverage of CZTS HTL. On the contrary, the increase in I_{SC} is also confirmed by the overall external quantum efficiency (EQE) values and integrated photocurrent of CZTS PSC. In addition, I-V curve for PSCs with CZTS HTL showed smaller hysteresis as compared to PSCs with spiro-OMeTAD HTL.



Figure 2.4: n-i-p planar architecture used to fabricate PSC with CZTS HTL¹⁰⁶.

Regarding the CZTS-perovskite interface, Ultraviolet-Visible (UV-Vis) spectroscopy has not shown any significant absorption peak shift and change of spectral onset, suggesting the unlikeliness of Cu/Pb exchange between CZTS HTL and the perovskite layer²⁰⁵. Furthermore, the light absorption for CZTS PSC increased dramatically in the entire visible region (400-850 nm), due to the absorption by CZTS HTL. Besides that, X-ray diffraction (XRD) analysis showed both CZTS and perovskite retain their tetragonal structure and the incorporation of CZTS HTL does not affect the crystallinity of the perovskite layer. Also, cross-sectional and surface morphology images from scanning electron microscopy (SEM) showed homogenous deposition of CZTS HTL, along with smoothening of the perovskite layer by CZTS NPs filling. In addition, Nyquist plot from electrochemical impedance spectroscopy (EIS) suggested CZTS HTL can improve the interfacial contact between the perovskite layer and Au electrode, prohibiting electron-hole recombination which may result in the loss of holes²⁰⁶. Similarly, Bode-phase plot also confirmed the role of CZTS HTL in reducing charge recombination, with the calculation of electron lifetime (3.5 ms) close to spiro-OMeTAD HTL (3.8 ms). This study demonstrated the versatility of CZTS, not just as an absorber layer, but also as a transport layer; which showed similar performance to conventional spiro-OMeTAD HTL.

A study on band gap tuning and its effect on the V_{OC} of n-i-p perovskite (CH₃NH₃PbI₃) solar cell, using CZTS quantum dots (QDs) HTL was done by Yuan et al.²⁰⁷. CZTS QDs were synthesized using the hot injection method, and the band gap was tuned by replacing sulphur (S) with selenium (Se). SEM images showed the CZTS HTL uniformly covered the perovskite layer; preventing the silver (Ag) electrode layer from touching, causing short circuit. This evidence also supported the reproducibility claim of the PSC fabrication. Besides that, the resistivity test showed that replacement of S with Se greatly decreased the film resistivity²⁰⁸, from 112.3 Ω ·cm to 4.56 Ω ·cm. Surface photovoltage spectroscopy (SPS) signal revealed an increase, after the incorporation of CZTS HTL, indicating a higher efficiency of charge separation at the interface. In addition, SPS signal on the PSC with CZTSe HTL showed a higher increase, suggesting the improvement of charge transport process in the HTL, which plays an important role in charge separation. Furthermore, cyclic voltammetry (CV) showed CZTSe possesses larger valence offset, which sufficiently favours holes injection from the perovskite layer, compared to CZTS. **Figure 2.5** shows the energy level alignment of PSCs with both HTLs.



Figure 2.5: Energy level alignment of PSC with CZTS and CZTSe HTLs²⁰⁷.

Recombination rate was also studied using EIS and revealed that PSC with CZTSe HTL presented lower recombination resistance

(R_{rec}; due to its fast transport process, inducing higher recombination rate. Regarding PSC performance, I-V analysis was done; CZTS and CZTSe HTLs showed comparable I_{SC} (~19 mA/cm²), but a slightly higher FF for PSC with CZTSe HTL (62.1% compared to 60.5%), due to smaller R_s (25.1 Ω compared to 34.8 Ω). However, V_{OC} is significantly lower for PSC with CZTSe HTL (0.808 V compared to 0.945 V), which leads to a decrease in PCE (9.72% compared to 10.72%). The Voc losses of PSC with CZTSe HTL was attributed to the variation of the HTL's Fermi level (Ef), which was mainly influenced by the band-edge shift of valence band and the recombination at perovskite-HTL interface²⁰⁹. Besides that, theoretical calculation demonstrated the achievable Voc of only 1.0 V for PSC with CZTSe HTL as compared to CZTS HTL (1.3 V). In addition, the narrow band gap of CZTSe (1.14 eV compared to 1.64 eV) may induce a maximum band-edge shift of valence band (V_b) loss of 300 mV in the fabricated device. This work demonstrated the possibility of band gap tuning of CZTS for a better fit in its role as an HTL. Also, this study provided evidence on the crucial role of band-edge shift in HTL towards Voc losses in PSC, which is often ignored.

A study on p-i-n perovskite (CH₃NH₃PbI₃) solar cell, applying ligand engineered CZTS NPs synthesized by high-temperature arrested precipitation in the coordinating solvent²¹⁰ was done by Khanzada et al.107. Long-chain oleylamine (OLA) ligand on CZTS NPs was successfully stripped and replaced with tetrafluoroborate ion $(BF_4)^{211}$. functionalized by weakly coordinating and further solvent, dimethylformamide (DMF), as represented in Figure 2.6. Results showed the absorbance of both stripped and unstripped NPs are similar, with a band gap of 1.5 eV, confirming their identical optical properties. Besides that, transmission electron microscopy (TEM) showed both NPs to be spherical with particles size of 5.46±1.1 nm (unstripped) and 5.15±1.0 nm (stripped). Structural analysis from XRD showed the kesterite CZTS peaks for both NPs, with calculated crystallite size of 6.3 nm (unstripped) and 5.6 nm (stripped), in agreement with TEM observations. Raman spectroscopy further confirmed the phase purity of CZTS for both NPs, with a slight presence of cubic CZTS phase. In addition, fast Fourier transform analysis also showed crystallographic orientations of kesterite CZTS with a tetragonal unit cell. Furthermore, high-resolution TEM (HR-TEM) revealed that the stripped CZTS NPs

possesses higher crystallinity with no evidence of defects, lattice deformation, and amorphous phase or secondary phases.

Polydispersity coefficient (σ) and inter-particle distances were also determined for both NPs; $\sigma = 0.20$ with 1.54 ± 0.38 nm inter-particle distance (unstripped) and $\sigma = 0.19$ with 0.98±0.26 nm inter-particle distance (stripped). The decrease in inter-particle distance of stripped CZTS NPs indicates the successful stripping of OLA ligand. In addition, Fourier-transform infrared (FTIR) spectroscopy revealed a reduction on several organic bonds' peaks; proving the removal of majority of surface organic ligands. Besides that, space charge limited current (SCLC) measurement revealed the hole mobility of stripped CZTS NPs $(3.4x10^{-2} \text{ cm}^2/\text{V}\cdot\text{s})$ is three order magnitude higher than its unstripped counterpart ($7.7 \times 10^{-5} \text{ cm}^2/\text{V} \cdot \text{s}$). Dark and photoconductivity also showed a significant difference (higher than three orders of magnitude) for stripped and unstripped CZTS NPs, which can be explained by substantially higher carrier mobility, due to improved particle-to-particle contact. Furthermore, PSCs fabricated applying the stripped CZTS NPs as HTL showed increased performance ($I_{SC} = 20.7$ mA/cm^2 , $V_{OC} = 0.92$ V, FF = 81%, PCE = 15.4%) with enhanced reproducibility compared to its unstripped counterpart ($I_{SC} = 18.1$ mA/cm^2 , $V_{OC} = 0.88$ V, FF = 77%, PCE = 12.2%). The impressive enhancement in FF is due to enhanced mobility and subsequent higher conductivity of the stripped CZTS NPs, further decreasing Rs from 1.01 $\Omega \cdot cm^2$ to 0.88 $\Omega \cdot cm^2$. Moreover, there's no observed significant anomalous hysteresis on the fabricated PSCs, thanks to the inverted pi-n architecture. This study showed the success of low-temperature CZTS NPs synthesis, with further application of said NPs as HTL in PSC; showing improvement in the performance.



Figure 2.6: Schematic representation of the OLA ligand removing from CZTS NPs surface¹⁰⁷.

There's also a study on n-i-p perovskite (CH₃NH₃PbI₃) solar cell, applying orthorhombic wurtzite CZTS NPs as HTL. Zuo et al.¹⁰⁸ synthesized wurtzite CZTS NPs using a low-cost, sol-gel method and deposited on the perovskite layer to act as HTL. They also fabricated PSC with spiro-OMeTAD HTL as comparison. Results from XRD and energy- dispersive X-ray spectroscopy (EDS) showed that the CZTS NPs are polycrystalline with a wurtzite structure, showing an atomic ratio of 2.05:1:1:4.05, confirming that CZTS NPs were successfully synthesized. Besides that, UV-Vis spectroscopy (Figure 2.7) of the deposited CZTS NPs film on perovskite showed a significant improvement of light absorption in the visible spectrum compared to its organic counterpart, due to the absorption of CZTS NPs, having a relatively small bandgap of 1.49 eV. PSC with CZTS HTL demonstrated a PCE of 13.41%, calculated from V_{OC} of 0.962 V, I_{SC} of 22.43 mA/cm², and FF of 62%. Meanwhile, PSC based on spiro-OMeTAD HTL showed Voc of 0.974 V, Isc of 23.01 mA/cm², and FF of 56%, leading to a PCE of 12.72%.

It was found that the crystallization and crystal-plane orientation, especially a more preferential in-plane orientation of the (1 1 0) plane of a perovskite film could improve the corresponding device performance²¹². Grazing incidence X-ray diffraction (GIXRD) revealed that perovskite film on CZTS NPs has a higher and sharper perovskite (1 1 0) diffraction peak, indicating a higher crystallization quality, thus contributing to the improvement in PSC performance. In addition, it was found that the hysteresis of PSC with CZTS NPs HTL (16.3%) is significantly lower than spiro-OMeTAD HTL (29.0%), pointing out a better effect on the hole transporting, a dramatic improvement in the charge extraction and reduced recombination^{106,213}. This study demonstrated the advantage of using low-cost, wurtzite CZTS as HTL in PSC as compared to the widely used organic spiro-OMeTAD HTL, with better performance and lower hysteresis.

Muhammad Ubaidah Syafiq bin Mustaffa – Alternative uses of CZTS thin films for energy harvesting



Figure 2.7: UV–Vis absorption spectra of different layers combination of PSC¹⁰⁸.

A study was conducted by Patel et al.⁶⁷ regarding the use of CZTS NPs synthesized using open air sol-gel method as HTL in an ni-p perovskite (CH₃NH₃Pb_{1-x}Sn_xI_{3-y}Cl_y) solar cell, and compared with an organic spiro-OMeTAD HTL PSC. Results showed that aging time during CZTS NPs synthesis affects the size of NPs obtained; the longer the aging time, the bigger the size of CZTS NPs (Figure 2.8) due to agglomeration. Besides that, SEM and dynamic light scattering (DLS) revealed the NPs to be spherical in nature. Since the study was on the use of CZTS NPs as HTL, smaller size NPs are preferable. In addition, band gap for the CZTS NPs was determined to be 1.52 eV. Phase purity of synthesized CZTS NPs was confirmed with XRD and Raman spectroscopy, with XRD showing peaks of kesterite CZTS, and no peaks associated with impurities such as ZnS, and Cu₂SnS₃ from Raman spectroscopy. The deposited CZTS NPs film was revealed to be very dense and uniform. PSC fabricated with CZTS NPs HTL showed PCE of 9.21%, with 19.23 mA/cm² $I_{SC},\,760$ mV V_{OC} and 63% FF. On other hand, PSC fabricated with spiro-OMeTAD HTL showed 9.88% PCE, with 17.94 mA/ cm² I_{SC}, 810 mV V_{OC}, and 68% FF.

There is a significant trade-off observed in I_{SC} (increase) and FF (decrease) between PSCs with CZTS HTL and spiro-OMeTAD HTL. FF is a function of the maximum power output (P_m), V_{OC} and I_{SC}^{214} . Besides that, FF is also influenced by R_S (should be low), shunt resistance (R_{sh}, should be high) and recombination charge transfer resistance (R_{ct}, should be high)²¹⁵. EIS revealed that achieved R_{ct} for PSC with CZTS HTL is marginally smaller, suggesting lower recombination resistance, thus, leading to a depreciation in FF. In addition, lower hysteresis effect is observed for CZTS HTL PSC (11.59%) than spiro-OMeTAD HTL PSC (19.98%). Furthermore, stability test was done on both PSCs with CZTS and spiro- OMeTAD HTLs. They exhibited excellent stability (> 98%) for the first 72 h. Further stability test done after 168 h revealed that PSC with CZTS HTL outperformed its organic counterpart, by retaining 75% of its initial efficiency. Much later, both showed efficiency degradation at a similar rate. Although the efficiency is slightly lower, this study managed to prove the advantage of CZTS NPs as HTL in PSC, with less hysteresis and superior stability.



Figure 2.8: Particle size distribution graph for CZTS NPs with different aging times⁶⁷.

Ashebir et al.⁶⁹ reported a work on CZTS NPs, prepared using molecular precursor solution method, as HTL in a p-i-n perovskite (CH₃NH₃PbI₃) solar cell. The deposited CZTS film showed XRD peaks correspond to kesterite CZTS, without secondary phases. In addition, Raman spectroscopy showed a peak for the A1 symmetry mode due to the symmetric vibration of S atom in CZTS²¹⁶ at 330 cm⁻¹. Besides that, XPS results demonstrated the chemical states of +1, +2, +4, and -2 of Cu, Zn, Sn, and S respectively in the film, which agrees with the element states of CZTS. Also, XPS results revealed the atomic ratio of Cu:Zn:Sn:S to be 2.0:0.8:0.9:4.1, which is close to the stoichiometric ratio of 2:1:1:4 of CZTS. Furthermore, SEM images showed the film consists of compact 10-20 nm CZTS NPs, without voids penetrating the film. The absorption coefficient of the as-prepared film is measured to be higher than 10^4 cm⁻¹ in the visible region, with the band gap of ~1.48 eV. Different CZTS HTL thicknesses and their effect on the device performance were studied in this work. Results showed that a decrease in CZTS HTL thickness causes a significant increase in Isc and incident photon-to-current conversion efficiency (IPCE), with no observable change in V_{OC} and FF. PSC with CZTS HTL of 97 nm thickness showed the best photovoltaic performance (Figure 2.9), with I_{SC} of 9.70 mA/cm², V_{OC} of 0.82 V, FF of 76.10% and PCE of 6.02%.

The decrease in photovoltaic performance of PSC with thick CZTS HTL originated from the reduction of Isc and IPCE values. This is due to the seemingly high absorption coefficient of CZTS film, which is higher than 10^4 cm⁻¹ in the visible region (specifically below 550 nm); causing the incident illumination intensity to be attenuated when passing through the CZTS HTL, leading to the reduced light intensity that can be absorbed by the perovskite layer. Besides that, they also fabricated a PSC with PEDOT:PSS HTL as a reference. They found that PSC with PEDOT:PSS HTL showed much lower efficiency (4.28%) than their best CZTS HTL PSC. In addition, the stability test revealed that PSC with CZTS HTL retained 87% of initial efficiency after 43 days of storage in N₂ atmosphere, with a stabilized power output over a period of 95 s, as compared to complete deterioration to zero after the storage in N₂ atmosphere for 35 days, for PSC with PEDOT:PSS HTL. This work managed to demonstrate the advantage of CZTS HTL for PSC, as opposed to its organic counterpart, in terms of device performance and stability.



Figure 2.9: I-V curve of PSC with 97 nm CZTS HTL. Inset shows the SEM image of the main device structure⁶⁹.

A recent work by Khattak et al.²¹⁷ modelled and simulated n-ip perovskite (CH₃NH₃SnI₃) solar cells with several quaternary semiconducting materials, including CZTS and CZTSe. They used SCAPS-1D "solar cell capacitance simulator" software for device modelling and simulated under 1.5 AM illumination spectrum. Results revealed that HTL with valence band (E_v) lower than the absorber showed better device performance, with good V_{OC} and I_{SC} , due to larger built-in potential (Vbi). Therefore, Cu₂FeSnS₄ (CFTS) as HTL gave the smallest V_{OC} and I_{SC} values, due to its high E_V compared to the absorber. Furthermore, CFTS also showed a higher recombination current compared to other HTLs. This is due to positive valence band offset (+VBO), leading to a higher built-in potential at the absorber-HTL interface than negative valence band offset (-VBO). In addition, they also found that high +VBO may lead to a decrease in Isc due to impediment of holes flow towards the back contact. Thus, it is necessary for HTL to possess a moderate +VBO. The simulation results shown in Figure 2.10 revealed that CZTSe HTL showed the highest PCE (19.43%), with V_{OC} , I_{SC} , and FF values of 0.86 V, 29.16 mA/cm², and 77.13% respectively.

The same authors also found that increase in HTL thickness didn't affect the I-V characteristic of the device but optimized to 0.1 μ m. Furthermore, an increase in absorber thickness showed an I_{SC} with

a seemingly constant Voc. This is due to the absorption of longer wavelength photon, causing an increase in photogenerated carriers and thickness effect on the quantum efficiency of the device, thus increasing FF and PSC. But, after reaching optimal thickness (0.5 µm), Isc remains constant. In addition, they also studied the effect of carrier doping in HTL, finding that doping concentration in HTL does not significantly affect the functional parameters of the device. However, acceptor doping of the absorber layer influenced the I-V characteristic of the device, thus affecting its performance. Increasing doping concentration causes I_{SC} to decrease and V_{OC} to increase, thus, affecting overall efficiency. The optimum value taken for acceptor doping was 1x10¹⁶ cm⁻³. Further increase in doping concentration leads to larger band bending at the absorber-buffer interface, causing an increase in interface recombination, which is detrimental to the device performance. This work provided crucial information on the parameters needed for quaternary semiconductors such as CZTS and CZTSe to be a good HTL.



Figure 2.10: I-V characteristics of different HTLs for PSC; CMTS (Cu₂MgSnS₄), CFTS (Cu₂FeSnS₄), CZTS (Cu₂ZnSnS₄), CZTSe (Cu₂ZnSnSe₄), CNTS (Cu₂NiSnS₄), CBTS (Cu₂BaSnS₄)²¹⁷.

Several of the studies done showed interesting results with PCE of the fabricated PSCs exceeding 10% (Wu et al., Yuan et al., Khanzada

et al., and Zuo et al.). Effects of device architecture and surface modification of CZTS on PSC performance can be discussed from the studies. Wu et al. and Khanzada et al. synthesized CZTS NPs using the hot-injection method, with OLA as ligand, but Khanzada et al. stripped the ligand from the surface of CZTS NPs before applying it as HTL. Significant improvement on FF can be observed on PSC with ligand-stripped CZTS NPs, showing the detrimental effect of organic ligand on CZTS HTL. Besides that, Khanzada et al. also applied different PSC architecture (p-i-n planar), compared to Wu et al. (n-i-p planar). There's no observable hysteresis on p-i-n PSC, while 22.4% of hysteresis can be seen on n-i-p PSC, showing inverted p-i-n architecture helps in preventing hysteresis on PSCs.

In addition, different structures of CZTS (kesterite and wurtzite) as HTL have been studied by Wu et al. and Zuo et al. respectively, applying similar materials and architecture. Wurtzite CZTS HTL showed a slight improvement in PSC performance compared to its kesterite counterpart, which can be due to its higher carrier concentration and lower resistivity⁹³. Furthermore, the tuneability of band gap is also studied, experimentally and theoretically. Yuan et al. narrowed the bandgap of CZTS film by replacing S with Se, showing improvement in I_{SC} and FF, but a decrease in V_{OC} and PCE. However, the simulated theoretical study made by Khattak et al. showed an overall performance improvement of CZTSe compared to CZTS. This contradiction shows that there is still a lot of aspects such as recombination rate and band-edge shift, that can be studied for CZTS to reach its full potential as HTL in PSCs.

To summarize, the discussion on research done regarding the use of CZTS HTL in PSCs mainly shows its advantage compared to the conventionally used HTLs, such as spiro-OMeTAD and PEDOT:PSS. **Table 2.2** shows a summary on research done on PSCs utilizing CZTS as HTL. A noteworthy advantage of CZTS HTL is the ability to at least retain or even improve PSC performance, due to its good electrical properties. Besides that, CZTS possesses superior stability, for the absence of organic components in its structure. In addition, it also provides an easier, low-cost, abundant, and less toxic alternative of HTL for PSCs. However, studies on the application of CZTS as HTL are still in preliminary stages, and there are clearly rooms for significant improvement.

Year published	Researchers	PSC architecture	Perovskite	HTL	Voc (V)	I _{SC} (mA/cm ²)	FF (%)	PCE (%)	Notes
2015	Wu et al.	n-i-p planar	CH ₃ NH ₃ PbI ₃	Kesterite CZTS NPs	1.06	20.5	59	12.8	Experimental study
2016	Yuan et al.	n-i-p mesoporous	CH ₃ NH ₃ PbI ₃	Kesterite CZTS QDs	0.95	18.8	61	10.7	Experimental study
				Kesterite CZTSe QDs	0.81	19.4	62	9.7	Experimental study
2016	Khanzada et al.	p-i-n planar	CH3NH3PbI3	Ligand-stripped CZTS NPs	0.92	20.7	81	15.4	Experimental study
				Ligand-unstripped CZTS NPs	0.88	18.1	77	12.2	Experimental study
2018	Zuo et al.	n-i-p planar	CH ₃ NH ₃ PbI ₃	Wurtzite CZTS NPs	0.96	22.4	62	13.4	Experimental study
2018	Patel et al.	n-i-p planar	$\begin{array}{c} CH_{3}NH_{3}Pb_{1-x}S\\ n_{x}I_{3-y}Cl_{y} \end{array}$	Kesterite CZTS NPs	0.76	19.2	63	9.2	Experimental study
2019	Ashebir et al.	p-i-n planar	CH ₃ NH ₃ PbI ₃	Kesterite CZTS NPs	0.82	9.7	76	6.0	Experimental study
2019	Khattak et al.	ttak et al. n-i-p planar	CH ₃ NH ₃ SnI ₃	Kesterite CZTS	0.82	29.3	72	17.5	Simulation
				Kesterite CZTSe	0.86	29.2	77	19.4	study

Table 2.2: Summary of research done on CZTS as HTL in PSC.

2.3. Perspective

Since studies done regarding CZTS HTL showed potentials in improving the performance and stability of PSCs, further research in this area is highly recommended. A detailed study on the effects of grain growth of CZTS HTL on PSC performance can be done since CZTS with larger grains is favourable to increase current carrier concentration and improve electron transmission²¹⁸. It has also been reported that different structures of CZTS have a significant difference in their electrical properties^{83,219}; thus, it may also be beneficial to study different structures of CZTS and their effects on PSC performance, in a more comprehensive manner. Furthermore, the effects of CZTS HTL doping on PSC performance present a lucrative study opportunities, since doping changes the surface energy landscape, further affecting the work function²²⁰. In addition, CZTS band gap can be easily tuned by the incorporation of Se, as seen in the discussion. Thus, fine band gap tuning of CZTS HTL for a more efficient hole injection shows a very interesting study opportunity to further improve PSC performance.

2.4. Outlook

Due to its good electrical properties, superior stability, ease of fabrication and band tuning, and elemental abundance, CZTS can be considered as a candidate to replace conventional organic HTL such as spiro-OMeTAD and PEDOT:PSS in PSC. However, more studies are necessary, on the effects of grain growth, different structures of CZTS, doping, and fine band gap tuning. As mentioned in this review article, these research suggestions will greatly help CZTS to better fit its new role, as HTL in solar cell applications. Thus, extensive studies on this subject are strongly encouraged, since it has opportunities to pave a new pathway to the development of high-performance PSCs with superior stability, further directing them towards commercialization.

Declaration of Competing Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement: The authors thank Dr. Mohd Sukor Su'ait for his help in conceptualizing this review article, along with some helpful comments and suggestions. Also, the authors thank Dr. Eleonora Isotta for helpful comments and suggestions. This work is supported by the Autonomous Province of Trento within the framework of the programmatic Energy Action 2015–2017.

3. Thermoelectric generator (TEG) based on thin films of CZTS

Some part of this section was taken and edited (under a CC BY license) from¹¹⁵: Thermoelectric properties of CZTS thin films: effect of Cu-Zn disorder. Eleonora Isotta, Ubaidah Syafiq, Narges Ataollahi, Andrea Chiappini, Claudia Malerba, Sally Luong, Vanira Trifiletti, Oliver Fenwick, Nicola M. Pugno, and Paolo Scardi. *Physical Chemistry Chemical Physics*. 2021, **23**, 13148-13158. DOI: https://doi.org/10.1039/D1CP01327K

Please cite any appropriate part of this section as specified above.

Abstract

This chapter will discuss the use of CZTS thin films for TEG application, in term of fabrication, materials properties and preliminary performance analysis. Due to its abundance of elements and non-toxicity, CZTS is considered as a sustainable "green" material and will be used as p-leg, coupled with aluminium-doped zinc oxide (AZO) as n-leg, in TEG with horizontal architecture, demonstrating the feasibility of using this material in thermoelectric technology. Some discussion regarding transport properties of CZTS thin film has been published in a recent article by our group¹¹⁵. Meanwhile, discussion on performance and optimization of CZTS thin film TEGs will be a part of an article that is currently being drafted.

3.1. Introduction

Kesterite CZTS (reference formula Cu_2ZnSnS_4) has attracted the attention of the photovoltaic community as a promising alternative to $Cu(In,Ga)Se_2$ (CIGS) absorber layers in thin film solar cell technology⁶⁵. The highest achieved efficiency in CZTS thin-film solar cells to date is 12.6 %⁴⁴, despite the Shockley-Queisser limit indicating a theoretical efficiency of up to 32.4 %¹⁰⁴. Reasons for this sluggish development can be, to a certain extent, traced back to the material itself. Among the defects present in CZTS, Cu-Zn antisites have been recently studied in detail due to the discovery of the order–disorder phase transition, which is second order and reversible. Over the critical temperature of 533 K, the Cu⁺ and Zn²⁺ cations which share the same crystallographic plane, randomize their positions^{221,222}. Thermal history influences the amount of Cu-Zn disorder, but perfect order is

thermodynamically impossible to obtain above 0 K. For this reason, regardless of the material composition, a certain number of Cu_{Zn} - Zn_{Cu} antisites form at ambient temperature. Despite the role of these antisites on the photovoltaic performance still being the object of debate^{45,49,223–226}, it has been recently suggested that tail-related detrimental defects are associated with growth conditions providing a slow ordering rate and thus highly disordered samples²²⁶.

In recent years, CZTS in bulk form has been investigated for high temperature thermoelectric (TE) applications^{114,154,204,227–230}. Little has been explored regarding thermoelectricity in CZTS thin films, despite the vast knowledge acquired in the past two decades on their fabrication^{231–233}. TE energy conversion exploits the Seebeck effect, the development of a voltage gradient in a material as a consequence of an applied temperature difference⁷². The TE figure of merit, $zT = \alpha^2 T / \rho \kappa$, is used to assess the performance, where α is the Seebeck coefficient, ρ the electrical resistivity, T the absolute temperature, and κ thermal conductivity. It was recently shown in bulk CZTS that Cu-Zn disorder can be beneficial for TE performance by boosting Seebeck coefficient without penalizing electrical conductivity. This was achieved through a modification in the band structure, leading to flatter and more converged bands. This was correlated with the higher crystallographic symmetry of the disordered tetragonal phase with respect to the ordered^{204,229}.

Therefore, two key-points can be underlined: (i) the Cu-Zn disorder can be indicative of poor quality of the as-grown absorber in photovoltaic devices, thus making it essential to be identified, quantified and understood and (ii) this same disorder might instead be exploited in other applications such as thermoelectricity^{204,229,234} and tuneable electronics^{235–237}, pointing to attractive directions for micro power generation^{238,239} and sensing²⁴⁰, as well as micro-electromechanical systems (MEMS)²⁴¹.

TEGs are solid state devices with no moving parts that can convert heat into electricity, or vice versa. They have many attractive features such as long life, no moving parts, no emissions of toxic gases, low maintenance, and high reliability⁷⁷. The basic unit of a TEG consists of a p-type and an n-type thermoelement connected electrically in series by a conducting strip. This basic unit or a "TE module" can also be employed as the building blocks for the construction of a TEG, which consists of several TE modules connected electrically in series but thermally in parallel. TEGs utilize heat flow across a temperature gradient to power an electric load through the external circuit, where temperature difference, ΔT , provides the voltage from the Seebeck effect, while the heat flow drives the electrical current, which will determine the power output²⁴². The rejected heat will be removed through a heat sink.

TEGs have been widely used in the field of energy harvesting, semiconductor cooling, and temperature sensors⁸¹. Though the performance of the thermoelectric materials and generators has been improved in the past decades, it is still far from commercialization due to high cost of preparing high performing TEGs, which dominantly based on expensive and rare materials such as tellurium (Te) and bismuth (Bi), along with complex preparing methods⁸². Thus, fabrication of a low-cost TEG with an acceptable performance can also be a way forward for this technology. One way to fabricate low-cost TEGs with improved performance is by reducing dimensionality to obtain thin film TEGs, which reportedly improves the thermoelectric properties of materials due to low-dimensional quantum confinement and a much lower lattice thermal conductivity^{243–245}. Also, the free charge carriers of thin films have longer average free layer that can reduce the scattering which leads to faster response speed⁸².

Thin film horizontal TEGs possess low dimension and weight, which is competitive in the application of micro-machines and miniature accessories, such as micro-coolers, micro-power generators, and micro-sensors. In addition, with the possibility of deposition onto flexible substrates, bendable thin film TEGs offer promise to function in wearable devices meeting the need for future developments. Moreover, transparent thin films like zinc oxide (ZnO), can also be utilized in TEGs architecture for external glass wall or electronic screen. Furthermore, the structure of thin films allows more ways to enhance the thermoelectric properties, as is known, interface between the film and the substrate, or the ones between multilayers, exert significant effect on the grain growth, which deserves systematic studies in their link with TEGs performance²⁴⁶.

In this chapter, CZTS thin film will be used alongside AZO thin film for TEG with horizontal architecture. Discussion will be made on the fabrication, TE materials properties, TEG preliminary performance analysis, and some routes for optimization. To our best knowledge, this a novel attempt on fabricating TEGs with CZTS as p-type material. CZTS can be considered as a "green" material, due to its low-cost, abundance of elements, and non-toxicity, making it one of the energy harvesting materials with low environmental impact. Thus, the use of CZTS in thin film TEG application will provide a lucrative opportunity for this technology to grow sustainably.

3.2. Materials and methods

3.2.1.Synthesis of CZTS nanoparticles ink

Copper (II) chloride dihydrate (CuCl₂·2H₂O, >99.0 %), zinc chloride (ZnCl₂, >98.0 %), and tin (II) chloride (SnCl₂,98 %) were purchased from Sigma-Aldrich Inc. and dehydrated in vacuum at 473 K. Sulphur (S), oleylamine (OLA, 70 %), toluene (99.9 %), and ethanol (>99 %) were also purchased from Sigma-Aldrich Inc. and used without further purification.

A CZTS nanoparticles ink was prepared according to the method described by Syafiq et al. $^{123}\!\!$, with a modified setup for N_2 and vacuum lines as shown in Figure 3.1. Precursor solutions were prepared by mixing 0.538 g of CuCl₂·2H₂O, 0.414 g of ZnCl₂ and 0.410 g of SnCl₂ into a 250 ml three-necked round-bottomed flask containing 6.6 ml of oleylamine (OLA). OLA was added to work both as a solvent and as a capping agent for the CZTS nanoparticles. The solution was stirred and heated in a silicon (Si) oil bath. The mixture was heated to 403 K, then degassed and refilled with N₂ several times before being kept under vacuum. Next, 10 ml of S/OLA 1 M solution (prepared by dissolving 0.449 g S in 10 ml OLA) was rapidly injected in the solution upon reaching ~543 K. The mixture was kept at 543 K for 30 min after the injection and then cooled naturally to room temperature. The obtained suspension of nanoparticles was washed with a mixture of 5 ml toluene and 25 ml ethanol and centrifuged for 10 min at 12000 rpm to separate the solvent from the nanoparticles. Finally, the CZTS nanoparticles were extracted by removing the supernatant, dispersed in toluene, and sonicated to obtain an ink with the desired concentration.



Figure 3.1: Modified setup for CZTS nanoparticles ink synthesis.

3.2.2.CZTS thin film deposition and thermal treatment The deposition was done on soda-lime glass (SLG) substrates. SLG substrates were manually cleaned with soap, treated with concentrated potassium hydroxide (KOH) in ethanol, rinsed with distilled water and ethanol, and finally dried using compressed air. 1 g/ml CZTS nanoparticle ink was used for the deposition of CZTS thin films with different thicknesses. For a thinner film, deposition was done by a spincoating method (50 ml ink at 2000 rpm for 30 s). Deposition of thicker films was done by the doctor-blade technique.

Two stages of thermal treatment were performed on the deposited CZTS thin films¹³³. The thermal treatment was done inside a quartz tube furnace connected to separate vacuum, N₂, and exhaust lines. For the first stage, the tube was pumped down to \sim 3.0 °⁻¹ mbar. The tube was then flushed with N₂ to purge the system of residual air, and the temperature ramped up to 773 K at 3 K/min and kept stable for 1 hour. The annealed sample was then cooled down to room temperature in a continuous flow of N₂. CZTS thin films were then taken out to be annealed in the presence of an excess amount of S for

the second stage of thermal treatment. The procedure for the second thermal treatment follows the first, except for the annealing temperature which was set at 833 K^{219} .

3.2.3.CZTS/AZO TEG fabrication

For thin film CZTS/AZO TEG fabrication, three components; CZTS pleg, AZO n-leg, and silver (Ag) metal contacts were deposited on 1 mm cleaned SLG substrates as shown in **Figure 3.2a**. The TEG was designed so that the thermoelectric components must be electrically connected in series but thermally in parallel. The depositions were done using Kapton tape as deposition mask. First, CZTS thin film legs were deposited using spin-coating method as described above. The Kapton mask was removed before thermal treatment and reapplied for AZO thin film deposition. Paper sheets were used on top of the film to prevent the deposited film to stick on the Kapton tape.



Figure 3.2: **a)** Schematic design of thin film CZTS/AZO TEG, **b)** Fabricated thin film CZTS/AZO TEG.

Next, AZO thin film legs were deposited via radio frequency (RF) magnetron sputtering of AZO source (98 % zinc oxide, ZnO and 2 % aluminium oxide, Al₂O₃). The conditions for the sputtering are as follows; 50 W power, 13.56 MHz frequency, ~5.0 x 10^{-6} mbar minimum working pressure, and 30.8 % Argon, Ar atmosphere. The sputtering time was fixed to 10 minutes to obtain the desired thickness of ~250 nm. Again, the Kapton mask was removed and reapplied for Ag metal contact deposition, including the use of a paper sheet on top of the films to prevent sticking to the Kapton tape.

Finally, Ag metal contact was deposited via thermal evaporation of ~0.49 g silver pellets (99.99 % purity). The pellets were put on a tungsten heating boat inside the evaporation chamber along with target attached upside-down at the top with ~26 cm of distance in between. The chamber was then vacuumed up to ~1.5 x 10^{-5} mbar minimum working pressure, before evaporating the silver onto the target via Joule heating using 90 A current. The evaporation stopped once the silver pellets fully evaporated, giving ~300 nm thickness. Kapton mask was removed, and a small dab of silver paint was applied at both terminals to increase robustness of contacts during measurement. **Figure 3.2b** shows the fully fabricated thin film CZTS/AZO TEG.

3.2.4. Thin films characterization

The morphology of CZTS thin film samples was observed by scanning electron microscopy (SEM), using a JEOL JSM-7001F FEG- SEM (JEOL, Tokyo, Japan) equipped with an energy-dispersive X-ray spectroscopy detector (EDXS, Oxford INCA PentaFETx3, Oxford, UK). Observations were made at 10.0-15.0 keV electron beam energy with a working distance of 5-10 mm. Surface morphology images were acquired in a top-down configuration, whereas a cross-sectional analysis was performed by putting the cross-section of the film on a 90° stub. On the other hand, surface morphology of AZO thin film was observed top-down using SEM (COXEM EM-30AX, Daejeon, Korea), equipped with EDXS detector. Observation was made at 20.0 keV electron beam energy with a working distance of 10.2 mm.

Thin films thicknesses were measured using Dektak 3 Surface Profilometer with 2.5 μ m radius diamond-tip stylus, passing 2 mm scan range crossing the film with a perpendicular "trench". X-ray diffraction (XRD) patterns of CZTS thin film were collected in Bragg-Brentano geometry with a Cu-K_a radiation source (Rigaku PMG, Tokyo, Japan) for 1.5 mm and 30 mm-thick samples, obtained respectively by spincoating and by doctor-blade deposition from the same ink. A Rietveldrefinement of XRD data was performed with the TOPAS 7 software package, with the aid of Whole Powder Pattern Modelling (WPPM) macros for size analysis^{247,248}. Meanwhile, XRD pattern of AZO thin film was collected in Bragg-Brentano geometry with Co-K_a radiation source (Bruker D8 Discover, Karlsruhe, Germany). Raman spectra were collected using a LabRAM Aramis (Horiba Jobin-Yvon) equipped with an optical microscope and a 100X objective. Diode-pumped solid-state laser sources of 532 nm and 785 nm were used for the excitation of the Raman signal that was detected with an air-cooled charge-coupled device. The overall acquisition time was 10 s with laser powers of 1.8 mW (532 nm) and 2.3 mW (785 nm). A fit of the Raman spectra was performed with the software PM2K²⁴⁹. Although specifically designed for the analysis of XRD patterns, the software is easily adapted to the analysis of Raman spectra, using a set of nine Lorentzian peaks. The background was removed to allow comparison with previous works²²¹. Discussion regarding Raman analysis were presented in the aforementioned published article¹¹⁵ and the thesis of Eleonora Isotta²⁵⁰.

Electrical resistivity and Seebeck coefficient measurements were performed with a Linseis LSR-3 Meter in the temperature range 320-720 K. Resistivity was measured in 2-contact configuration with the aid of a thin film adapter for high resistance samples. The Seebeck coefficient was measured in 4-contact configuration with Pt standard and a temperature gradient of 10 K. In-plane thermal conductivity measurements were performed with a Linseis Thin Film Analyser. The measurement is done on a suspended Si₃N₄ membrane incorporated on a pre-patterned measurement chip using a quasi-steady state $3-\omega$ method. The measurement, which is performed under vacuum and in the dark, is described in detail elsewhere^{251–253}.

3.2.5. Thin film CZTS/AZO TEG performance measurement Two TEG performance measurements were done on the fabricated thin film CZTS/AZO TEGs, open circuit voltage versus temperature difference (V_{OC} vs Δ T) and current-voltage-power (I-V-P) measurements. V_{OC} vs Δ T measurement was done to measure the highest voltage that can be generated at varied temperature difference of hot side (T_h) and cold side (T_c) of the TEG. **Figure 3.3a** shows the setup used to conduct the V_{OC} vs Δ T measurements. The voltage measurements were taken from the voltmeter, while temperature differences were captured by a thermal camera. T_h and T_c were taken on the glass substrate, near the TEG legs as shown in **Figure 3.3b**. This is due to the differences in materials' emissivity, making the value taken on neither TEG legs nor metal contacts correct. This assumption was validated when a TEG was coated in graphite coating and gave a homogenous reading throughout T_h and T_c , as shown in **Figures 3.3c**, **d**. Furthermore, due to the TEG thin film architecture, the heat flow was dominated by the substrate, giving the assumption on T_h and T_c more reliable.





For I-V-P measurement, the schematic of the setup can be seen in **Figure 3.4a**, while **Figure 3.4b** shows the real setup that is prepared in the laboratory. An ammeter and variable resistor were connected in series, while a voltmeter was connected in parallel, with respect to the TEG. This measurement can be explained by a reduction in voltage when a current is allowed by controlling the setup resistance using the variable resistor. In open circuit, the setup resistance is infinity and the TEG's highest voltage will be produced but there will be no power output due to zero current. By reducing resistance, current will increase, leading to an increase in power output. Upon reaching zero resistance, current will achieve maximum due to short circuit, while voltage and power output will drop to zero. From this measurement, the TEG's highest achievable power can be calculated as P=VI.



Figure 3.4: a) Schematic setup for I-V-P measurement, b) Picture of I-V-P measurement setup.

- 3.3. Results and discussion
 - 3.3.1.Morphological and structural characterization of CZTS thin film

SEM images show CZTS thin films prepared by spin-coating (SC samples from here on, **Figures 3.5a**, **b**) consist of ~1.0 μ m thick uniform layer of CZTS nanoparticles with some micrograins (>1.0 μ m in size) scattered on top. The films deposited via doctor-blade method (DB samples from here on, **Figures 3.5c**, **d**) are much thicker (~26 μ m) but possesses similar surface morphology.



Figure 3.5¹¹⁵: **a, b)** Cross-section and surface SEM images of SC CZTS thin film, **c, d)** Cross-section and surface SEM images of DB CZTS thin film.

The elemental composition from EDXS analysis (**Figure 3.6**, referring to SC sample) shows a Zn-rich Cu-poor composition for the whole film (site 1), classified as A-type CZTS²⁵⁴. The S content is close to stoichiometric, a feature that is believed to promote a faster Cu-Zn ordering (or disordering) through a higher density of cation vacancies, according to a recent study²²⁶. Large and isolated particles (>5 μ m in size) on top of the SC film (site 2) show a Cu-rich stoichiometry that could originate from a partial segregation of Cu from the film.



	Atomic percentage (%)					
	Cu	Zn	Sn	S		
Site 1	23.8 (8)	14.5 (8)	12.2 (4)	49.4 (5)		
Site 2	40.6 (1)	19.0 (1)	11.3 (5)	29.1 (5)		
Stoichiometric	25.0	12.5	12.5	50.0		

Figure 3.6¹¹⁵: Atomic percentage of each element in SC CZTS thin film from EDXS.

XRD patterns, data modelling and corresponding residuals for the SC and DB samples are plotted in Figure 3.7. The two sets of XRD data have been refined simultaneously, modelled with the same tetragonal *I-42m* kesterite phases. The samples present a good phase purity, with a minor fraction (3.0 (1) % of total weight) of chalcocite Cu₂S, that was speculated to be connected with the superficial Cu-rich particles seen in SEM. A macro to correct for the absorption of thin films²⁵⁵ has been used for the SC sample, that, based on the decay of intensity at larger angles, estimates a sample thickness of $\sim 1.8 \ \mu m$ (assuming a theoretical density of 4.56 g/cm³), in good agreement with the SEM images. For this film, two broad peaks have been added to model the contribution of the SLG substrate, visible in the lower angle region of the pattern. This was not necessary for the DB film, as the radiation is entirely absorbed within the thicker kesterite laver. The modelling of the kesterite peak profiles requires two CZTS phase fractions, a coarser one (with mean crystal-domain size estimated in the range of 0.5 (2) µm) and a finer one (around 10.0 (8) nm), to account for the large dispersion of crystal-domain dimensions in the samples, a feature suggested by the SEM images in Figure 3.5. A similar bimodal distribution was observed by TEM in a previous study on kesterite powders, although prepared using a different technique^{154,204}. Cell parameters display a slight variation between the two phases and are estimated as a = 5.437 Å and c = 10.848 Å for the coarser phase, and a = 5.416 Å and c = 10.896 Å for the finer phase. For both samples, the coarser kesterite phase appears to be present in the largest fraction (65% and 73% in total weight of kesterite, respectively for the SC and DB sample).



Figure 3.7¹¹⁵: XRD data refinement for SC and DB films. The two patterns have been simultaneously refined with a unique kesterite model.

3.3.2. Thermoelectric properties of SC CZTS thin film The electronic transport properties (electrical resistivity, ρ , and Seebeck coefficient or thermopower, α , which combined give the Power Factor, PF= α^2/ρ) for a slowly cooled and a quenched spin-coated film are visible in **Figures 3.8a-c**. The slowly cooled sample presents high ρ and low α values in the lower-temperature range. Between 450 K and 550 K the thermopower displays a sharp rise, remaining then high for higher temperatures. The electrical resistivity presents a generally decreasing trend, evidencing the semiconducting nature, only perturbed by a small kink in the range 450 K-550 K.

These features were believed to be the hallmark of the orderdisorder transition. Indeed, as predicted by ab-initio simulations, and experimentally verified in recent work of our group^{204,229}, the phase transition from ordered *I-4* to disordered *I-42m* tetragonal CZTS leads to a modification in the electronic band structure which strongly affects the electronic properties. With the disordered structure, the top three valence bands tend to converge significantly and to become flatter. Band convergence (or band degeneracy N_V) is a known mechanism in thermoelectricity that can decouple the trends of α and $\rho^{256,257}$. Moreover, the increased flatness of the bands happening with disorder imply higher inertial effective mass of charge carriers m_I^* . Both these effects are significant as the Seebeck coefficient is directly proportional to the density of state effective mass $m_{DOS}^* = N_V^{2/3} m_I^*$. For these reasons, the transition from ordered to disordered CZTS, happening around 533 K, leads to a sharp rise in the thermopower.

At the same time, the electrical resistivity trend does not present significant features at the transition. A reason for this could be that on one side band degeneracy can improve the carrier concentration, on the other, the increased m_1^* implies a lower carrier mobility. This double effect (improved carrier concentration and decreased carrier mobility) has been experimentally verified on bulk polycrystalline samples²²⁹ and leads to a not-much-affected electrical resistivity trend. On the other hand²⁰⁴, thermal analyses show that the observed sharp rise in Seebeck coefficient is associated with a second-order and reversible transition)²²¹.

The electronic properties of the slowly cooled and quenched spin-coated films are in accordance with previous theoretical predictions and experimental observations on bulk polycrystalline samples. A research group derived an order parameter, S for the Cu-Zn order-disorder transition using Raman spectroscopy analysis^{221,258,259}, where S=1 means perfect order, whereas S=0 stands for full disorder. Indeed, for the slowly cooled sample the progressive development of Cu-Zn disorder leads to the enhancement of the Seebeck coefficient, localized in the proximity of the transition critical temperature of 533 K. The effect is particularly evident as the sample starts from an ordered condition (S estimated ~ 0.7). The electrical resistivity trend is instead not much affected, likely due to the reasons explained above. The quenched sample, given its initial disordered state (S estimated ~0.2), exhibits a "disordered behavior" straight from the beginning of the measurement, with lower electrical resistivity and higher Seebeck coefficient values. The trends consistently show reduced transitionspecific features around 533 K, as allegedly little of the sample is performing the order-disorder transition.

It is noticeable that, with respect to these, CZTS thin film measurements present a sharper variation of electronic properties at the transition compared to bulk CZTS²⁰⁴, possibly due to different kinetics

of the phase transition. This can also originate from a different temperature-homogenization between bulk and thin film samples. As expected, the disordered quenched sample presents a higher PF and a weaker dependence on temperature. Figure 3.8d shows a measurement of thermal conductivity κ for an as-deposited sample. κ was measured by the in-plane 3Ω method on a thin (~100 nm) Si₃N₄ membrane incorporated on a silicon chip with pre-patterned electrodes. This allows in-plane measurements, in line with the other thermoelectric measurements in Figure 3.8.



Figure 3.8¹¹⁵: **a)** Electrical resistivity, ρ , **b)** Absolute Seebeck coefficient, α , **c)** Power Factor, PF, for SC CZTS thin film. A sample after slow cooling (blue, squared markers), initially in more ordered state, and a sample after quenching from 623 K post-annealing (orange, circular markers), in more disordered state, **d)** Thermal conductivity, κ , for the as-deposited SC CZTS sample.

SEM images in **Figure 3.9** on corresponding chip- and SLGas-deposited samples do, however, show that both films are continuous and pin-hole free. No major morphological differences are observed. Also, smaller grain size than in the films on SLG was confirmed, as expected from the lower annealing temperature. In addition, the delicate nature of the Si_3N_4 membrane prevented the thermal treatment of the sample at 833 K, as this damaged the measurement chips. The analysis was therefore limited on as-deposited samples (only with annealing at 373 K, performed in a glove box). The absence of treatment and different surface energy of the Si_3N_4 compared to SLG may induce different morphology in the film and different S.





From the literature, CZTS is known to possess a comparably low κ^{114} , among TE materials, and indeed the film presents values below 0.6 W/mK. This is associated in general to the crystallographic complexity of CZTS, often subject to cation disorder, and additionally, in this specific case, to the high density of grain boundaries associated with the lack of thermal treatment. In addition, geometrical measurement of density was performed on some thermally treated SC samples. The mass of the film was measured by the difference in weight before and after scratching it away from the substrate. Large-area samples (~25mm x 25mm) were used. Measured weights were around three orders of magnitude higher than the sensitivity of the scale. Thicknesses were measured with a profilometer. The average sample density is ~98 %, with the lowest measured value of 93 %.
To estimate zT for the thermally treated films, calculation was done on the thermal conductivity from the lattice component (κ_L) of a polycrystalline bulk sample, corrected for the electronic component (κ_e) of the thin film sample. This discussion was presented in the aforementioned published article¹¹⁵ and the thesis of Eleonora Isotta²⁵⁰. An estimate of zT can be obtained from the PF data and the calculated values of κ and yield a maximum of ~0.035 at 673 K, as shown in Figure 3.10¹¹⁵. Despite the considerable level of uncertainty in the calculation (speculated as at least ~ 30 %), this estimation of zT is in literature values for accordance with pristine CZTS bulk samples^{114,227,228,230}. The quenched sample presents comparatively higher values of PF, especially in the low temperature range, suggesting that Cu-Zn disorder can overall lead to a higher TE performance.



Figure 3.10¹¹⁵: Measured thermal conductivity, κ , for the as-deposited sample, and estimated κ , with lattice component (κ_L), and figure of merit *zT* for thermally treated CZTS sample.

3.3.3.Morphological and structural characterization of AZO thin film

SEM image at x100 magnification as shown in **Figure 3.11** showed that the AZO thin film covers the entirety of the substrate in a continuous and homogenous manner, with some observed pinholes that might be due to the presence of small contaminants during the sputtering. In addition, EDXS analysis from the same SEM image showed the elemental composition of the fabricated AZO. Results showed the general elemental composition of the sample. High amount of zinc (Zn) and oxygen (O), with some traces of Aluminium (Al) are to be expected due to the initial composition of the source. In addition, the stoichiometry of O is higher than expected in the film, along with some trace amount of silicon (Si) and calcium (Ca). This is due to the beam penetration depth being higher than the AZO thin film thickness, making the analysis include some part of the SLG.

	Element	Norm. Mass Percent (%)	Atomic Percent (%)
	Zn	66.91	35.94
	0	24.74	54.31
	Al	1.02	1.33
	Si	5.33	6.66
	Ca	2.01	1.76

Figure 3.11: SEM image and elemental composition from EDXS of fabricated AZO thin film.

In addition, the XRD pattern in **Figure 3.12** shows that the fabricated AZO possesses ZnO-like zincite phase (JCPDS 75-1526) with a preferred orientation perpendicular to the (002) planes. The narrow peaks indicate a well-crystalline film, with no observable peaks of spurious phases.



Figure 3.12: XRD pattern of AZO thin film.

3.3.4. Thermoelectric properties of AZO thin film

The electronic transport properties (α , ρ , and PF) of fabricated AZO are shown in **Figure 3.13a**. Absolute Seebeck coefficient, α , showed a negative value, indicating that the majority charge carriers in the fabricated AZO thin film are electrons, thus proving it to be an n-type semiconductor⁷². The value of α increases linearly in the negative direction as temperature increases, with the highest recorded value of ~80 μ V/K at ~560 K, which in agreement with other reported values²⁶⁰. On the other hand, resistivity of AZO thin film decreases with temperature, showing a semiconducting behaviour, with the lowest recorded value of ~31.0 μ Ω·m at ~560 K, which is also within the same magnitude and similar values as others^{260,261}. From these two transport properties, PF can be calculated, showing an expected trend of increasing values with temperature up to ~1.95 μ W/K²·cm at ~560 K.

Furthermore, **Figure 3.13b** shows in-plane thermal conductivity, κ , measurement, along with calculation of zT based on the obtained results. The values of κ measured to be in the range of 5.2-5.9 W/m·K at 333-533 K temperature range are in agreement with

literature^{262–266}. However, small deviation may occur due to different grain sizes which reportedly affect thermal conductivity^{267,268}. From α , ρ , and κ obtained, *zT* was calculated and estimated to yield an increasing *z*T value at increased temperature up to ~0.016 at 533 K.



Figure 3.13: **a)** Absolute Seebeck coefficient (α), electrical resistivity (ρ), Power Factor (PF), **b)** thermal conductivity (κ), and *zT* of AZO thin film.

3.3.5.Thin film CZTS/AZO TEG preliminary performance analysis

 V_{OC} vs ΔT measurement gives information on the maximum voltage that can be generated by the fabricated thin film CZTS/AZO TEG at specific ΔTs . A hotplate was used to control T_h with a 10 K increment from 323 K up to 523 K, while T_c was kept in ambient temperature with a metal plate as heat sink. However, the measured ΔTs did not read as the set temperature of T_h and T_c due to substrate buffer and poor heat sink setup. Substrate buffer might be affecting the efficiency of the TEG, since some of the heat will be wasted on the substrate²⁴². Nevertheless, result in **Figure 3.14** shows a linear fitting of voltage increase as ΔT increases, with a maximum voltage generated ~87 mV at ΔT of ~443 K.



Figure 3.14: V_{OC} vs ΔT measurement of thin film CZTS/AZO TEG.

Figure 3.15 shows the I-V-P measurements of thin film CZTS/AZO TEG at different Δ Ts. For simplicity, the figures were separated into I-V (Figure 3.15a) and I-P (Figure 3.15b) plots. The temperatures indicate the hotplate temperature that were set on T_h side of the TEG, since it is the main component in determining ΔT , as discussed before. The I-V plots are linear for all the Δ Ts, with the slope of the plots indicating the TEG's internal resistance. The values of the slopes reduced from 28.6 k Ω at 323 K to 14.9 k Ω at 523 K, which agrees with the reduction of resistivity at elevated temperature of a semiconductor for both CZTS and AZO as discussed in 3.4.2 and 3.4.4, neglecting the small resistivity effect of Ag metal contacts^{269,270}. On the other hand, the I-P plot shows a curve with a maximum power output at the peak, where it normally occurs at the point where the load resistance matches the device resistance²⁷¹. Results show that higher ΔT produces higher power output, that reaches up to ~55 nW at 523 K. For a thin film TEG with only two p-n couples, though the obtained power was quite low, it shows a significant improvement as compared to other

Muhammad Ubaidah Syafiq bin Mustaffa – Alternative uses of CZTS thin films for energy harvesting

TEGs in term of power output 271 and the use of "greener" materials 82,234,272 .



3.3.6. Optimization of thin film CZTS/AZO TEG From the results obtained, optimization of thin film CZTS/AZO TEG was studied with collaboration from the Polytechnic University of Catalonia (UPC), Spain. Two aspects studied for the optimization were the effect of p-n couples' number and CZTS thin film's quality. Regarding the number of p-n couples, thin film CZTS/AZO TEG was fabricated with the improved architecture as shown in Figures 3.16. This architecture enables a better use of the substrate, with addition of two more p-n couples. In addition, the optimized TEG also uses Curich, Zn-poor CZTS thin film prepared by sputtering. Cu-rich, Zn-poor CZTS reportedly improves PF, while reducing κ which will improve its overall zT^{230} . Besides that, sputtered CZTS thin film gives a better advantage as compared to spin-coated CZTS thin film in term of better composition control, high density film, full use of raw materials, deposition site freedom, contamination-free, and high film uniformity²⁷³.



Figure 3.16: **a)** Schematic design of optimized thin film CZTS/AZO TEG, **b)** Fabricated optimized thin film CZTS/AZO TEG.

The sputtered Cu-rich, Zn-poor CZTS thin film was prepared by UPC, and some preliminary analyses were done on the samples before being used for the fabrication of the optimized CZTS/AZO TEG. Profilometer measurement showed the thin film was ~2.21 μ m in thickness. SEM-EDXS result in **Figures 3.17a**, **b** revealed that the film consists of a uniform layer of CZTS grains with a slight Cu-rich, Znpoor stoichiometry, as intended. In addition, 785 nm Raman spectroscopy in **Figure 3.17c** detected a clear presence of Sn_2S_3 secondary phase, that might be due to off-stoichiometry. The amount of this phase increases at the sample edge. Besides that, 532 nm Raman spectroscopy in **Figure 3.17d** shows an insignificant amount of Cu_xS phase that may also exists just on the sample surface.



Figure 3.17: a) SEM image, b) EDXS result, c) 785 nm Raman spectrum, and d) 532 nm Raman spectrum of sputtered Cu-rich, Zn-poor CZTS thin film.

In addition, the electronic transport properties (α , ρ , and PF) of the sputtered CZTS thin film was also studied, as shown in **Figure 3.18**. The value of α increases linearly as temperature increases, with the highest recorded value of ~295 μ V/K at ~560 K, which is of similar value to the fabricated SC CZTS thin film from nanoparticles ink. However, there is no sharp rise in α , indicating the presence of a major Cu-Zn disorder within the sample. On the other hand, resistivity of the sputtered CZTS thin film decreases with temperature, showing a semiconducting behaviour, with the lowest recorded value of ~880.0 $\mu\Omega$ ·m at ~560 K. The values obtained was ~500 % lower, as compared to the disordered SC CZTS thin film (~5000 $\mu\Omega$ ·m at ~560 K), showing a superior conductivity.

Besides that, PF was calculated from α and ρ shows an expected trend of increasing values with temperature up to ~0.98 μ W/K²·cm at ~560 K. PF value can be used as a precursory parameter to estimate the thermoelectric performance of a material. Thus, by comparing PF of the sputtered CZTS thin film and SC CZTS thin film from nanoparticles





Figure 3.18: Absolute Seebeck coefficient (α), electrical resistivity (ρ), and Power Factor (PF) of sputtered CZTS thin film.

Preliminary performance analysis of the fabricated optimized CZTS/AZO TEG showed some improvements that can be discussed. V_{OC} vs ΔT measurement in Figure 3.19a shows an increase of voltage generated at a specific ΔT by around twofold. This can be explained by the TEG's electrical connection that is in series, making the doubling of p-n couples in the TEG architecture doubles the voltage that can be generated. Besides that, I-V-P plot in Figure 3.19b shows a significant increase in the maximum power output, from ~55 nW to ~350 nW. The main factor that contributes to this improvement is the low TEG's internal resistance due to better CZTS thin film quality with reduced resistivity, as discussed before. Supposedly, an increase in p-n couples though will lead to an increase in the voltage generated, will also increase the TEG's internal resistance that will balance out the power output. However, due to low resistivity of the sputtered CZTS thin film combined with its Cu-rich, Zn-poor stoichiometry, the TEG's internal resistance was kept low (~9.1 k Ω) compared to the spin-coated CZTS/AZO TEG (~14.9 k Ω) with only two p-n couples. This result shows that one of the main criteria in improving a TEG's performance lies in improving (i.e., reducing) its internal resistance, while maintaining high voltage generation.



Figure 3.19: a) V_{OC} vs Δ T, and b) I-V-P measurements of spin-coated CZTS/AZO TEG and sputtered CZTS/AZO TEG

3.4. Conclusions

This chapter presents some preliminary results on the use of CZTS thin films for TEG application. CZTS nanoparticles ink was synthesized via hot-injection method and a thin film was deposited onto SLG substrate by spin-coating followed with thermal treatment. Fabricated CZTS thin films (p-legs) was then coupled with AZO thin films (n-legs) with Ag thin film as metal contacts to form CZTS/AZO TEG. Besides that, thermoelectric transport properties for both CZTS and AZO thin films were also discussed. TEG's preliminary performance results revealed that the fabricated CZTS/AZO TEG performs well with a maximum power output of ~55 nW at ~443 K Δ T. In addition, TEG performance was further studied with some attempts of optimization, with results indicated the possibility of TEG improvement (>600 % in power output) by increasing voltage generated while maintaining low internal resistance.

Granted, the huge performance improvement was mainly due to the adoption of sputtered films, but consideration must also be given to the prospect of a scaled-up production. Even though sputtering technology can be scaled up, the operating and production costs are undeniably high, giving a bit of advantage for cheap and robust deposition technologies such as ink printing to thrive. However, as pointed out during the discussion, efforts must be done to improve thin film conductivity for a TEG to perform well, which is still ongoing. In conclusion, this chapter provides an insight of CZTS thin film to be a good and promising candidate for a "green" p-type material for TEG application.

4. Conclusions, perspectives, and ongoing activities

This thesis reports a versatile approach on the synthesis and fabrication of CZTS thin films, followed by the study of properties in relation to the fabrication parameters. A CZTS nanoparticles ink was successfully synthesized via the bottom-up approach of hot-injection, using metal chloride precursors, sulphur, and oleylamine. The synthesized ink was then used to fabricate CZTS thin films via spin-coating, followed by thermal treatments. It was found that CZTS thin films fabricated using lower concentration inks and higher spin rates were lower in thickness, higher in transmittance, and better in morphology. Besides that, the thermal treatment temperature affected the film's overall properties including surface morphology, crystal structure, transmittance behaviour, band gap energy, and electrical properties. An increase in thermal treatment temperature improved the degree of crystallinity and electrical properties, along with the observed phase change going from the less stable cubic and wurtzite structures to a more stable tetragonal structure, due to the decomposition of the ligand oleylamine. However, a high thermal treatment temperature may also lead to the formation of secondary phases like SnS, due to sulphur loss²⁷⁴, which is detrimental to the mobility of the carriers.

Besides that, this doctoral work explores the possibility of CZTS for alternative uses in energy harvesting, specifically transport layer and thermoelectric applications. Discussion on CZTS as a HTL in PSCs showed its potential in improving performance and stability, warranting high recommendation for further research in this area. For example, a detailed study on the effects of grain growth of CZTS HTL on device performance can be done, since CZTS with larger grains showed an increase in current carrier concentration and improved electron transmission²¹⁸. Moreover, studies done observed that different structures of CZTS possessed significant differences in electrical properties^{83,219}, which may benefit a comprehensive study on different structures of CZTS and their effects on device performance. Furthermore, the effects of CZTS doping and element substitution on device performance present lucrative research opportunities in fine tuning of CZTS's energy landscape to improve device performance. For example, doping was observed to change the surface energy landscape, further affecting work function²²⁰, while element substitution such as the incorporation of Se can easily tune CZTS's band gap^{101,174}.

Finally, the work done on CZTS for thermoelectric applications revealed that CZTS possessed suitable transport properties to be a potential p-type material in a TEG, where the Seebeck coefficient (α) increased and electrical resistivity (ρ) decreased with temperature, resulting in an increased power factor (PF). In addition, thermal conductivity (κ) keeps low throughout the temperature range, promoting a zT enhancement with temperature. Although the value is not significant, the use of a considerably "green" material with a vast potential for improvement¹¹⁴ gave some credit to justify the use of CZTS in this work. Moreover, the use of CZTS for thermoelectric applications was further continued in this doctoral work with the fabrication of a TEG using p-type CZTS coupled with n-type AZO, with silver metal contacts. Preliminary performance results showed a good performance of the fabricated device with a maximum power output of ~55 nW at ~170 K Δ T. Additionally, the device performance was further studied with some attempts of optimization including the number of p-n couples and CZTS thin film's quality. This increased the generated voltage while maintaining low internal resistance, revealing a >600% improvement in power output, with ~350 nW at similar ΔT .

In conclusion, this thesis provides a "new life" for CZTS in energy harvesting, despite the struggle in its use as absorber layer for thin film solar cells, with some prospects highlighted. Regarding synthesis and fabrication, compensation on sulphur, combined with a good environment and temperature control during the thermal treatment were found to be essential to obtain a high quality CZTS. Thus, research on facile, low-cost, and highly reliable methods to obtain high quality CZTS, comparable to the sputtering method, can be a good prospect for further studies. Besides that, CZTS was considered to be a potential candidate to replace conventional organic HTLs such as spiro-OMeTAD and PEDOT: PSS in PSCs due to its good electrical properties, superior stability, ease of fabrication and band tuning, and elemental abundance. In this regard, more studies are encouraged on the effects of grain growth, different CZTS structures, doping, and fine band gap tuning, to enable CZTS fits better in its new role, paving a new path for the development of high-performance PSCs with superior stability, further realizing it towards commercialization. Furthermore, this work also demonstrated the possibility of CZTS to be used in TEGs, along with some discussion and preliminary performance analysis. Although the huge performance improvement was mainly due to the

adoption of high-conductivity sputtered films, consideration must also be given to the prospect of a scaled-up production using a simpler and low-cost approach. Thus, a lot of efforts can still be done to improve CZTS thin film conductivity for device improvement, including but not limited to CZTS enhancement studies as mentioned above.

As discussed, this thesis provides introductory insights for CZTS to be used alternatively in energy harvesting. Thus, it is no wonder that there are ongoing works from the author and his colleagues, related to this work. Currently, there is a work under its way regarding the synthesis of a chalcogenide nanoparticles ink from ball-milled powders including copper tin sulphide (CTS), copper zinc tin selenide (CZTSe), and copper tin sulphide-selenide (CZTSSe). As of now, attempts have been made by mechanical mixing of the ball-milled powder with oleylamine for nanoparticles encapsulation before being dispersed in toluene. Dynamic light scattering (DLS) analysis as shown in **Figure 4.1** revealed that the nanoparticles are clumps of nano- up to micro-grains of the chalcogenides with uniform radii of ~3.67 μ m, ~0.37 μ m, and ~1.51 μ m for CTS, CZTSe, and CZTSSe, respectively.



Figure 4.1: DLS results for CTS, CZTSe, and CZTSSe nanoparticles inks.

For an ink suspension, the obtained sizes of the nanoparticles are quite big, which pose several challenges for the thin film fabrication. Bigger nanoparticles size translates to heavier mass, consequently increasing the sediment rate of the nanoparticles to the bottom of the ink, reducing the ink's stability. Besides that, the control of a film's thickness depends on the size of the nanoparticles. In theory, the lowest achievable thickness of a film will be determined by the size of nanoparticles. Therefore, bigger nanoparticles size limits the control of film thickness to be deposited. Even though there are workarounds for the posed challenges in this current work, such as sonication before deposition and increasing the film thickness, synthesis of a more stable ink with smaller nanoparticles size for better size control is important and will be subject of ongoing work. Nevertheless, the synthesized inks of CTS, CZTSe and CZTSSe were used for the fabrication of thin film TEGs.

In continuation from the first ongoing work, the study of TEGs from other p-type chalcogenides in the CZTS families, including CTS, CZTSe, and CZTSSe is also in progress. At present, different chalcogenides prepared using different preparation methods including hot-injection synthesis, ball-milling, and sputtering, have been used as p-type legs in the fabrication of thin film TEGs and preliminary device performances have been measured. Figure 4.2 shows the measured V_{OC} vs ΔT plot of the devices, showing a linear increase in voltage as ΔT increases. Preliminary observations show the effect of substrate thickness on ΔT , where thicker substrate (sputtered CZTSe, 2 p-n couples, 3 mm SLG) leads to lower ΔT , leading to a lower maximum voltage due to suppression of heat transfer to the active material²⁷⁵. Moreover, it is also observed that the addition of p-n couples by a factor of two doubles the amount of generated voltage, as discussed in Chapter 3. However, differences in the voltage generated by different chalcogenides and different preparation methods cannot be well explained yet. As far as experience leads, this might be due to the films' quality, dimension, thickness, and intrinsic properties of the materials. Presently, no conclusive remarks can be deduced, thus warranting further studies to be done on each materials' thermoelectric properties.



Figure 4.2: V_{OC} vs ΔT measurement of TEGs using different pchalcogenides.

In addition, I-V-P measurements were also done on the fabricated devices, as shown in Figure 4.3. It can be noted that devices with sputtered p-legs possess lower internal resistance (as can be seen by the lower slope) due to better quality of films, leading to higher current flow, which consequently leads to higher device performance. Besides that, the importance of sulphurisation during thermal treatment can also be observed in CTS samples, where sulphurised CTS performs exceptionally better compared to non-sulphurised CTS. Additionally, the performance of different p-type chalcogenides can be observed, where CZTSe-based devices perform better as compared to CZTS-, CTS-, and CZTSSe-based devices. However, comparisons based on current observations are unfair due to the absence of a well-defined geometrical constant in the measurement. Thus, the development of standardized parameters for performance comparison such as power density, power per unit area, and device efficiency, is important for this work to move forward. Further studies need to be done to understand the basis of device engineering, including materials' thermoelectric properties, preparation of film with good quality, and effects of film's quality on the device performance, to have a grasp on a way to fabricate devices with optimal performance.



Figure 4.3: I-V and I-P measurement plots of TEGs using different chalcogenides as p-legs.

Finally, geometrical optimization of the thin film TEG for performance improvement is also one of the ongoing works. A device's thermoelectric figure of merit (*ZT*) can be written as $ZT=S^2T/RK$, where *S* is the device's total Seebeck coefficient, *R* the device's electrical resistance, T the absolute temperature, and *K* device's thermal conductance, with an inverse relation of *R* and *K*. From the equation, it is obvious that *ZT* can be improved by reducing *R* and *K*, which are connected to the legs dimension and materials' properties. A basic model has been developed based on an article related to thin film Peltier cooler²⁷⁶, to predict the optimum dimension of p- and n-type materials based on the equation as shown below:

$$RK = \left(\frac{\rho_p}{w_p t_p} + \frac{\rho_n}{w_n t_n}\right) \cdot \left(\kappa_p w_p t_p + \kappa_n w_n t_n + \kappa_g w_g t_g\right)$$

where;

ρ is electrical resistivity,

 κ is thermal conductivity,

w is leg's width,

t is leg's thickness, and

Subscript p, n, and g indicate p-type, n-type, and glass substrate, respectively.

By fixing other parameters, **Figure 4.4** shows an example of a plot obtained from the model calculation, predicting the optimum width of CZTSe thin film to be deposited for obtaining a device with maximum *ZT*, which will translate to better performance. However, the model is still crude, lacking some variables to be considered such as metal contacts' electrical and thermal resistances, along with no accompaniment of experimental proof. Thus, more efforts are required in this work, which will provide a better theoretical understanding of the overall work and will help the advancement of CZTS-based TEGs and thermoelectricity in general.



Figure 4.4: Plot obtained from the optimization model for CZTSe's width in CZTSe/AZO thin film TEG.

5. Appendix

- 5.1. List of publications
 - 5.1.1.Syafiq, U., Ataollahi, N., DiMaggio, R. & Scardi, P. Solution-based synthesis and characterization of Cu₂ZnSnS₄ (CZTS) thin films. Molecules 24, 13 (2019).
 - 5.1.2.Syafiq, U., Ataollahi, N. & Scardi, P. Progress in CZTS as hole transport layer in perovskite solar cell. Sol. Energy 196, 399–408 (2020).
 - 5.1.3.Isotta, E., Syafiq, U., Ataollahi, N., Chiappini, A., Malerba, C., Luong, S., Trifiletti, V., Fenwick, O., Pugno, N. M. & Scardi, P. Thermoelectric properties of CZTS thin films: effect of Cu-Zn disorder. Phys. Chem. Chem. Phys. (2021).
- 5.2. Participation to schools and conferences
 - 5.2.1.6th International Conference on Multifunctional, Hybrid and Nanomaterials (HYMA 2019), Sitges, Spain, 11th-15th March 2019.
 - 5.2.2.Summer School on Organic Photovoltaic Systems (ISSOPVS 2019), Kavala, Greece, 1st-10th July 2019.
 - 5.2.3.10th European Kesterite+ Workshop and PhD day, Uppsala, Sweden, 20th-22nd November 2019.
 - 5.2.4.11th European Kesterite+ Workshop 2020, Online, 26th-27th November 2020.
 - 5.2.5.Advances in Energy Materials Mini-Symposium, Online, 5th January 2021.
 - 5.2.6.Rigaku XRD Forum, Online, 2nd-4th March 2021.

References

- 1. Ritchie, H. Energy mix. *Our World in Data* https://ourworldindata.org/energy-mix (2020).
- Cheek, L. 3 Reasons We Are Still Using Fossil Fuels | University of Arkansas Sustainability Blog. University of Arkansas Sustainability Blog https://wordpressua.uark.edu/sustain/3-reasons-we-are-stillusing-fossil-fuels/ (2020).
- 3. Hore-Lacy, I. *Nuclear Energy in the 21st Century*. (World Nuclear University Press, 2006).
- 4. Peter W. Kingsford. James Watt. *Encyclopedia Britannica* https://www.britannica.com/biography/James-Watt (2021).
- Tom Kool. The Complete History Of Fossil Fuels . *OilPrice.com* https://oilprice.com/Energy/Energy-General/The-Complete-History-Of-Fossil-Fuels.html (2020).
- 6. bp p.l.c. *Statistical Review of World Energy*. https://www.bp.com/content/dam/bp/businesssites/en/global/corporate/pdfs/energy-economics/statisticalreview/bp-stats-review-2020-full-report.pdf (2020).
- 7. Lang, O. The dangers of mining around the world. *BBC News* https://www.bbc.com/news/world-latin-america-11533349 (2010).
- 8. The seven most dangerous jobs in the energy sector. *Power Technology* https://www.power-technology.com/features/mostdangerous-jobs-in-the-energy-sector/ (2020).
- 9. Bell, F. G. & Donnelly, L. J. *Mining and its Impact on the Environment*. (CRC Press, 2006).
- 10. Butt, N. *et al.* Biodiversity risks from fossil fuel extraction. *Science (80-.).* **342**, 425–426 (2013).
- 11. The Advantages & Disadvantages of Fossil Fuels. *Inspire* https://www.inspirecleanenergy.com/blog/clean-energy-101/advantages-disadvantages-fossil-fuels (2020).
- 12. Denchak, M. Fossil Fuels: The Dirty Facts. *NRDC* https://www.nrdc.org/stories/fossil-fuels-dirty-facts#secburning (2018).
- Marsh, J. Disadvantages of Fossil Fuels. *EnergySage* https://news.energysage.com/disadvantages-fossil-fuels/ (2018).
- 14. Ritchie, H. & Roser, M. Energy. *Our World in Data* https://ourworldindata.org/energy (2020).
- Kariuki, D. Barriers to Renewable Energy Technologies Development. *Energy Today* https://www.energytoday.net/economics-policy/barriersrenewable-energy-technologies-development/ (2018)

doi:10.1515/energytoday-2018-2302.

- Moradiya, M. A. The Challenges Renewable Energy Sources Face. AZoCleantech.com https://www.azocleantech.com/article.aspx?ArticleID=836 (2019).
- 17. Stram, B. N. Key challenges to expanding renewable energy. *Energy Policy* **96**, 728–734 (2016).
- 18. Power Quality Issues in Renewable Energy Systems. *Electrical Academia* https://electricalacademia.com/electric-power/power-quality-issues-renewable-energy-systems/.
- Ezhiljenekkha, G. B. & Marsalinebeno, M. Review of Power Quality Issues in Solar and Wind Energy. in *Materials Today: Proceedings* vol. 24 2137–2143 (Elsevier Ltd, 2019).
- van Zalk, J. & Behrens, P. The spatial extent of renewable and non-renewable power generation: A review and meta-analysis of power densities and their application in the U.S. *Energy Policy* 123, 83–91 (2018).
- Singh, S. Renewable Energy Development: Challenges to Green Growth. *Greenbiz* https://www.greenbiz.com/article/renewable-energydevelopment-challenges-green-growth (2010).
- 22. Ashok, S., Fonash, S. J. & Fonash, R. T. Solar cell. *Encyclopedia Britannica* https://www.britannica.com/technology/solar-cell (2020).
- 23. Becquerel, E. Mémoire sur les effets électriques produits sous l'influence des rayons solaires. *Comptes Rendus L'Academie des Sci.* 9, 561–567 (1839).
- 24. Fritts, C. E. On a new form of selenium cell, and some electrical discoveries made by its use. *Am. J. Sci.* **s3-26**, 465–472 (1883).
- 25. 1940: Discovery of the p-n Junction. Computer History Museum https://www.computerhistory.org/siliconengine/discovery-ofthe-p-n-junction/.
- 26. Russel S. Ohl. Light-sensitive electric device. (1946).
- 27. Chodos, A. This Month in Physics History. *APS Physics* https://www.aps.org/publications/apsnews/200904/physicshist ory.cfm (2009).
- Sinton, R. A., Kwark, Y., Gan, J. Y. & Swanson, R. M. 27.5-Percent silicon concentrator solar cells. *IEEE Electron Device Lett.* 7, 567–569 (1986).
- 29. Cui, M. *et al.* Thermal analysis and test for single concentrator solar cells. *J. Semicond.* **30**, (2009).
- 30. Dimroth, F. et al. Wafer bonded four-junction

GaInP/GaAs//GaInAsP/GaInAs concentrator solar cells with 44.7% efficiency. *Prog. Photovoltaics Res. Appl.* **22**, 277–282 (2014).

- Takamoto, T., Kaneiwa, M., Imaizumi, M. & Yamaguchi, M. InGaP/GaAs-based multijunction solar cells. *Prog. Photovoltaics Res. Appl.* 13, 495–511 (2005).
- 32. King, R. R. *et al.* 40% efficient metamorphic GaInPGaInAsGe multijunction solar cells. *Appl. Phys. Lett.* **90**, 183516 (2007).
- 33. Yamaguchi, M. *et al.* Novel materials for high-efficiency III-V multi-junction solar cells. *Sol. Energy* **82**, 173–180 (2008).
- Narayanan, S., Wenham, S. R. & Green, M. A. 17.8-Percent Efficiency Polycrystalline Silicon Solar Cells. *IEEE Trans. Electron Devices* 37, 382–384 (1990).
- 35. Nakaya, H. *et al.* Polycrystalline silicon solar cells with Vgrooved surface. *Sol. Energy Mater. Sol. Cells* **34**, 219–225 (1994).
- Stupca, M., Alsalhi, M., Al Saud, T., Almuhanna, A. & Nayfeh, M. H. Enhancement of polycrystalline silicon solar cells using ultrathin films of silicon nanoparticle. *Appl. Phys. Lett.* 91, 063107 (2007).
- 37. Saliba, M. *et al.* Cesium-containing triple cation perovskite solar cells: Improved stability, reproducibility and high efficiency. *Energy Environ. Sci.* **9**, 1989–1997 (2016).
- 38. Troughton, J., Hooper, K. & Watson, T. M. Humidity resistant fabrication of CH3NH3PbI3perovskite solar cells and modules. *Nano Energy* **39**, 60–68 (2017).
- Arora, N. *et al.* Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%. *Science (80-.).* 358, 768–771 (2017).
- Irwin, M. D., Buchholz, D. B., Hains, A. W., Chang, R. P. H. & Marks, T. J. p-Type semiconducting nickel oxide as an efficiency-enhancing anode interfacial layer in polymer bulkheterojunction solar cells. *Proc. Natl. Acad. Sci. U. S. A.* 105, 2783–2787 (2008).
- Huang, J. H., Velusamy, M., Ho, K. C., Lin, J. T. & Chu, C.
 W. A ternary cascade structure enhances the efficiency of polymer solar cells. *J. Mater. Chem.* 20, 2820–2825 (2010).
- 42. Koppe, M. *et al.* Charge carrier dynamics in a ternary bulk heterojunction system consisting of P3HT, fullerene, and a low bandgap polymer. *Adv. Energy Mater.* **3**, 949–958 (2013).
- 43. Katagiri, H., Jimbo, K., Tahara, M., Araki, H. & Oishi, K. The influence of the composition ratio on CZTS-based thin film solar cells. *Mater. Res. Soc. Symp. Proc. Vol. 1165* **1165**, 1165-M04-01 (2009).

- Wang, W. *et al.* Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency. *Adv. Energy Mater.* 4, 1–5 (2014).
- 45. Malerba, C., Valentini, M. & Mittiga, A. Cation Disorder In Cu2ZnSnS4 Thin Films: Effect On Solar Cell Performances. *Sol. RRL* **1**, 1700101 (2017).
- 46. Santra, P. K. & Kamat, P. V. Tandem Layered Quantum Dot Solar Cells . Tuning the Photovoltaic Response with Luminescent Ternary Cadmium Chalcogenides Tandem Layered Quantum Dot Solar Cells . Tuning the Photovoltaic Response with Luminescent Ternary Cadmium Chalcogenides. (2012) doi:10.1021/ja310737m.
- 47. Todorov, T. *et al.* Perovskite-kesterite monolithic tandem solar cells with high open-circuit voltage Perovskite-kesterite monolithic tandem solar cells with high open-circuit voltage. **173902**, (2014).
- 48. Bailie, C. D. *et al.* Semi-transparent perovskite solar cells for tandems with silicon and CIGS. *Energy Environ. Sci.* **8**, 956–963 (2015).
- 49. Rey, G. *et al.* Ordering kesterite improves solar cells: A low temperature post-deposition annealing study. *Sol. Energy Mater. Sol. Cells* **151**, 131–138 (2016).
- 50. Best Research-Cell Efficiency Chart. *NREL* https://www.nrel.gov/pv/cell-efficiency.html (2021).
- 51. Adolf Münzer, K., Holdermann, K. T., Schlosser, R. E. & Sterk, S. Thin monocrystalline silicon solar cells. *IEEE Trans. Electron Devices* **46**, 2055–2061 (1999).
- 52. Chander, S. *et al.* A study on photovoltaic parameters of monocrystalline silicon solar cell with cell temperature. *Energy Reports* **1**, 104–109 (2015).
- Guo, X., Lu, G. & Chen, J. Graphene-Based Materials for Photoanodes in Dye-Sensitized Solar Cells. *Front. Energy Res.* 3, 1–15 (2015).
- 54. Islam, M. M. *et al.* CIGS solar cell with MBE-grown ZnS buffer layer. *Sol. Energy Mater. Sol. Cells* **93**, 970–972 (2009).
- Pan, Y. L. & Tai, C. C. Thickness and conductivity analysis of molybdenum thin film in CIGS solar cells using resonant electromagnetic testing method. *IEEE Trans. Magn.* 48, 347– 350 (2012).
- 56. Britt, J. & Ferekides, C. Thin-film CdS/CdTe solar cell with 15.8% efficiency. *Appl. Phys. Lett* **62**, 2852 (1993).
- 57. Tiwari, A. N. *et al.* CdTe solar cell in a novel configuration. *Prog. Photovoltaics Res. Appl.* **12**, 33–38 (2004).
- 58. Tao, J. et al. Co-electrodeposited Cu2ZnSnS4 thin-film solar

cells with over 7% efficiency fabricated via fine-tuning of the Zn content in absorber layers. *J. Mater. Chem. A* **4**, 3798–3805 (2016).

- Jayawardena, K. D. G. I. *et al.* 'Inorganics-in-organics': recent developments and outlook for 4G polymer solar cells. *Nanoscale* 5, 8411–27 (2013).
- 60. Salim, T. *et al.* Perovskite-based solar cells: impact of morphology and device architecture on device performance. *J. Mater. Chem. A* **3**, 8943–8969 (2015).
- 61. Yoo, J. J. *et al.* Efficient perovskite solar cells via improved carrier management. *Nature* **590**, 587–593 (2021).
- Kojima, A., Teshima, K., Shirai, Y. & Miyasaka, T. Organometal Halide Perovskites as Visible- Light Sensitizers for Photovoltaic Cells. *J Am Chem Soc* 131, 6050–6051 (2009).
- 63. Zhang, S. & Han, G. Intrinsic and environmental stability issues of perovskite photovoltaics. *Prog. Energy* **2**, 022002 (2020).
- 64. Mali, S. S. & Hong, C. K. p-i-n/n-i-p type planar hybrid structure of highly efficient perovskite solar cells towards improved air stability: synthetic strategies and the role of ptype hole transport layer (HTL) and n-type electron transport layer (ETL) metal oxides. *Nanoscale* **8**, 10528–10540 (2016).
- Syafiq, U., Ataollahi, N. & Scardi, P. Progress in CZTS as hole transport layer in perovskite solar cell. *Sol. Energy* 196, 399– 408 (2020).
- 66. Liu, T., Chen, K., Hu, Q., Zhu, R. & Gong, Q. Inverted Perovskite Solar Cells: Progresses and Perspectives. *Adv. Energy Mater.* **6**, 1–17 (2016).
- 67. Patel, S. B., Patel, A. H. & Gohel, J. V. A novel and cost effective CZTS hole transport material applied in perovskite solar cells. *CrystEngComm* **20**, 7677–7687 (2018).
- Seo, S., Jeong, S., Bae, C., Park, N. G. & Shin, H. Perovskite Solar Cells with Inorganic Electron- and Hole-Transport Layers Exhibiting Long-Term (≈500 h) Stability at 85 °C under Continuous 1 Sun Illumination in Ambient Air. Adv. Mater. 30, (2018).
- 69. Ashebir, G. Y. *et al.* Solution-processed Cu2ZnSnS4 nanoparticle film as efficient hole transporting layer for stable perovskite solar cells. *J. Phys. Chem. Solids* **129**, 204–208 (2019).
- 70. Li, X. *et al.* Perovskite solar cells employing an eco-friendly and low-cost inorganic hole transport layer for enhanced photovoltaic performance and operational stability. *J. Mater.*

Chem. A 7, 7065–7073 (2019).

- 71. Strohl, G. R. & Harpster, J. W. Thermoelectric power generator - Principles of operation. *Encyclopedia Britannica* https://www.britannica.com/technology/thermoelectric-powergenerator/Principles-of-operation (2007).
- 72. Seebeck, T. J. Ueber die magnetische Polarisation der Metalle und Erze durch Temperatur-Differenz. *Ann. Phys.* **82**, 133–160 (1826).
- Velmre, E. Thomas Johann Seebeck and his contribution to the modern science and technology. *BEC 2010 - 2010 12th Bienn*. *Balt. Electron. Conf. Proc. 12th Bienn. Balt. Electron. Conf.* 17–24 (2010) doi:10.1109/BEC.2010.5631216.
- 74. Peltier, J. C. A. Nouvelles Experiences sur la Caloricite des Courans Electriques. *Ann. Chim. Phys.* **56**, 371–386 (1834).
- 75. Thomson, W. Account of researches in thermo-electricity. *Proc. R. Soc. London* 7, 49–58 (1856).
- 76. Thomson, W. On a Mechanical Theory of Thermo-Electric Currents. *Proc. R. Soc. Edinburgh* **3**, 91–98 (1857).
- Bell, L. E. Cooling, heating, generating power, and recovering waste heat with thermoelectric systems. *Science* vol. 321 1457–1461 (2008).
- McFarlane, H. F. Historical Survey of Test Reactor Programs at INL Over 70 Years. in *Encyclopedia of Nuclear Energy* 26– 38 (Elsevier, 2021). doi:10.1016/b978-0-12-819725-7.00041-6.
- 79. *Power Sources for Remote Arctic Applications*. https://ota.fas.org/reports/9423.pdf (1994).
- Junior, O. H. A., Calderon, N. H. & Silva De Souza, S. Characterization of a thermoelectric generator (TEG) system for waste heat recovery. *Energies* 11, (2018).
- 81. Disalvo, F. J. Thermoelectric cooling and power generation. *Science* vol. 285 703–706 (1999).
- 82. Fan, P. *et al.* Low-cost flexible thin film thermoelectric generator on zinc based thermoelectric materials. *Appl. Phys. Lett.* **106**, (2015).
- 83. Al-Shakban, M. *et al.* The synthesis and characterization of Cu2ZnSnS4 thin films from melt reactions using xanthate precursors. *J. Mater. Sci.* **52**, 12761–12771 (2017).
- 84. Chen, S., Gong, X. G., Walsh, A. & Wei, S.-H. Crystal and electronic band structure of Cu2ZnSnX4 (X=S and Se) photovoltaic absorbers: First-principles insights. *Appl. Phys. Lett.* 94, 041903 (2009).
- 85. Chen, S., Yang, J. H., Gong, X. G., Walsh, A. & Wei, S. H. Intrinsic point defects and complexes in the quaternary kesterite semiconductor Cu2 ZnSnS4. *Phys. Rev. B - Condens.*

Matter Mater. Phys. 81, 35–37 (2010).

- Bakr, N. A., Khodair, Z. T. & Mahdi, H. I. Influence of Thiourea Concentration on Some Physical Properties of Chemically Sprayed Cu 2 ZnSnS 4 Thin Films. 5, 261–270 (2016).
- Aruna-Devi, R., Latha, M., Velumani, S. & Chávez-Carvayar, J. Á. Structural and optical properties of CZTS nanoparticles prepared by a colloidal process. *Rare Met.* 40, 2602–2609 (2021).
- Gonce, M. K. *et al.* Photocatalytic Hydrogen Evolution Based on Cu2ZnSnS4, Cu2ZnSnSe4, Cu2ZnSnSe4-xSx Nanofibers. *RSC Adv.* 5, 94025–94028 (2015).
- 89. Ricardo, C. L. A. *et al.* Chloride-based route for monodisperse Cu2ZnSnS4 nanoparticles preparation Chloride-based route for monodisperse Cu 2 ZnSnS 4 nanoparticles preparation. *J. Renew. Sustain. Energy* **7**, (2015).
- 90. Huang, S., Luo, W. & Zou, Z. Band positions and photoelectrochemical properties of Cu ₂ ZnSnS ₄ thin films by the ultrasonic spray pyrolysis method. *J. Phys. D. Appl. Phys.* 46, 235108 (2013).
- 91. Murata, M., Chantana, J., Ashida, N., Hironiwa, D. & Minemoto, T. Influence of conduction band minimum difference between transparent conductive oxide and absorber on photovoltaic performance of thin-film solar cell In fl uence of conduction band minimum difference between transparent conductive oxide and absorber on ph. *Jpn. J. Appl. Phys.* 54, 032301 (2015).
- 92. Kattan, N., Hou, B., Fermín, D. J. & Cherns, D. Crystal structure and defects visualization of Cu2ZnSnS4 nanoparticles employing transmission electron microscopy and electron diffraction. *Appl. Mater. Today* **1**, 52–59 (2015).
- 93. Li, M. *et al.* Synthesis of Pure Metastable Wurtzite CZTS Nanocrystals by Facile One-Pot Method. *J. Phys. Chem. C* **116**, 26507–26516 (2012).
- 94. Ahmad, R. *et al.* A comprehensive study on the mechanism behind formation and depletion of Cu2ZnSnS4 (CZTS) phases. *CrystEngComm* **17**, 6972–6984 (2015).
- 95. Islam, M. A., Aziz, A., Witjaksono, G. & N. Amin. Structural, Electrical and Optical Properties of Zn Rich CZTS Thin Film. *IEEE Student Conf. Res. Dev.* 16–17 (2013) doi:10.1109/SCOReD.2013.7002549.
- 96. Olgar, M. A., Altuntepe, A., Erkan, S. & Zan, R. Fabrication of Cu-rich CZTS thin films by two-stage process: Effect of gas flow-rate in sulfurization process. *J. Mol. Struct.* **1230**, 129922

(2021).

- 97. Liu, B. *et al.* Effect of Na doping on the performance and the band alignment of CZTS/CdS thin film solar cell. *Sol. Energy* **201**, 219–226 (2020).
- 98. Barati, M., Nouri, N. & Manavizadeh, N. Investigation of Bismuth Doping Effects on CZTS Properties: A Density Functional Theory Study. in 2020 28th Iranian Conference on Electrical Engineering, ICEE 2020 (Institute of Electrical and Electronics Engineers Inc., 2020). doi:10.1109/ICEE50131.2020.9261048.
- 99. Ma, C., Guo, H., Zhang, K., Yuan, N. & Ding, J. Fabrication of p-type kesterite Ag2ZnSnS4 thin films with a high hole mobility. *Mater. Lett.* **186**, 390–393 (2017).
- 100. Simya, O. K., Geetha Priyadarshini, B., Balachander, K. & Ashok, A. M. Formation of a phase pure kesterite CZTSe thin films using multisource hybrid physical vapour deposition. *Mater. Res. Express* 7, 016419 (2020).
- Shibayama, N., Zhang, Y., Satake, T. & Sugiyama, M. Modelling of an equivalent circuit for Cu₂ ZnSnS₄ - and Cu₂ ZnSnSe₄ -based thin film solar cells. *RSC Adv.* 7, 25347– 25352 (2017).
- 102. Laghfour, Z. *et al.* Sodium doping mechanism on sol-gel processed kesterite Cu2ZnSnS4 thin films. *Superlattices Microstruct.* **120**, 747–752 (2018).
- 103. Friedlmeier, T. M., Wieser, N., Walter, T., Dittrich, H. & Schock, H. W. Heterojunctions based on Cu2ZnSnS4 and Cu2ZnSnSe4 thin films. in *Proceedings of the 14th European Conference of Photovoltaic Science and Engineering and Exhibition* (1997).
- 104. Ki, W. & Hillhouse, H. W. Earth-Abundant Element Photovoltaics Directly from Soluble Precursors with High Yield Using a Non-Toxic Solvent. *Adv. Energy Mater.* 1, 732– 735 (2011).
- 105. Siebentritt, S. Why are kesterite solar cells not 20% efficient? *Thin Solid Films* **535**, 1–4 (2013).
- 106. Wu, Q. *et al.* Kesterite Cu2ZnSnS4 as a Low-Cost Inorganic Hole-Transporting Material for High-Efficiency Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* 7, 28466–28473 (2015).
- 107. Khanzada, L. S. *et al.* Effective Ligand Engineering of the Cu2ZnSnS4 Nanocrystal Surface for Increasing Hole Transport Efficiency in Perovskite Solar Cells. *Adv. Funct. Mater.* 26, 8300–8306 (2016).
- 108. Zuo, Y. et al. High-efficiency perovskite solar cells improved

with low-cost orthorhombic Cu 2 Znsns 4 as the hole-transporting layer. *Mater. Tehnol.* **52**, 483–486 (2018).

- Yokoyama, D. *et al.* H2 evolution from water on modified Cu2ZnSnS 4 photoelectrode under solar light. *Appl. Phys. Express* 3, 101202 (2010).
- Yang, W. *et al.* Molecular Chemistry-Controlled Hybrid Ink-Derived Efficient Cu2ZnSnS4 Photocathodes for Photoelectrochemical Water Splitting. *ACS Energy Lett.* 1, 1127–1136 (2016).
- 111. Tay, Y. F. *et al.* Solution-Processed Cd-Substituted CZTS Photocathode for Efficient Solar Hydrogen Evolution from Neutral Water. *Joule* **2**, 537–548 (2018).
- Shi, X. Y., Huang, F. Q., Liu, M. L. & Chen, L. D. Thermoelectric properties of tetrahedrally bonded wide-gap stannite compounds Cu2 ZnSn1-x Inx Se4. *Appl. Phys. Lett.* 94, 122103 (2009).
- 113. Chen, D. *et al.* Hot-Injection Synthesis of Cu-Doped Cu2ZnSnSe4 Nanocrystals to Reach Thermoelectric zT of 0.70 at 450 °c. *ACS Appl. Mater. Interfaces* 7, 24403–24408 (2015).
- 114. Isotta, E. *et al.* Origin of a Simultaneous Suppression of Thermal Conductivity and Increase of Electrical Conductivity and Seebeck Coefficient in Disordered Cubic Cu2ZnSnS4. *Phys. Rev. Appl.* 14, 064073 (2020).
- 115. Isotta, E. *et al.* Thermoelectric properties of CZTS thin films: effect of Cu-Zn disorder. *Phys. Chem. Chem. Phys.* (2021) doi:10.1039/d1cp01327k.
- 116. Singh, O. P., Sharma, A., Gour, K. S., Husale, S. & Singh, V. N. Fast switching response of Na-doped CZTS photodetector from visible to NIR range. *Sol. Energy Mater. Sol. Cells* 157, 28–34 (2016).
- Gour, K. S. *et al.* Nanostructured Cu2ZnSnS4 (CZTS) thin film for self-powered broadband photodetection. *J. Alloys Compd.* 735, 285–290 (2018).
- Li, W. *et al.* Coaxially enhanced photocarrier transport of a highly oriented Cu2ZnSnS4/ZnO photodetector through the nanoconfinement effect. *J. Mater. Chem. C* 8, 3491–3497 (2020).
- Shinde, N. M., Deshmukh, P. R., Patil, S. V. & Lokhande, C. D. Development of polyaniline/Cu2ZnSnS4 (CZTS) thin film based heterostructure as room temperature LPG sensor. *Sensors Actuators, A Phys.* 193, 79–86 (2013).
- 120. Gurav, K. V. *et al.* Cu2ZnSnS4 (CZTS)-based room temperature liquefied petroleum gas (LPG) sensor. *Sensors Actuators, B Chem.* **190**, 408–413 (2014).

- 121. Patil, S. J., Bulakhe, R. N. & Lokhande, C. D. Liquefied petroleum gas (LPG) sensing using spray deposited Cu2ZnSnS4 thin film. *J. Anal. Appl. Pyrolysis* 117, 310–316 (2016).
- 122. Jain, S., Verma, S., Singh, S. P. & Sharma, S. N. An electrochemical biosensor based on novel butylamine capped CZTS nanoparticles immobilized by uricase for uric acid detection. *Biosens. Bioelectron.* **127**, 135–141 (2019).
- 123. Syafiq, U., Ataollahi, N., DiMaggio, R. & Scardi, P. Solutionbased synthesis and characterization of Cu2ZnSnS4 (CZTS) thin films. *Molecules* 24, 13 (2019).
- 124. Nakayama, N. & Ito, K. Sprayed films of stannite Cu2ZnSnS4. *Appl. Surf. Sci.* **92**, 171–175 (1996).
- 125. Park, S.-N. *et al.* Nanostructured p-type CZTS thin films prepared by a facile solution process for 3D p-n junction solar cells. *Nanoscale* 7, 11182–11189 (2015).
- 126. Habas, S. E., Platt, H. A. S., van Hest, M. F. A. M. & Ginley, D. S. Low-Cost Inorganic Solar Cells: From Ink To Printed Device. *Chem. Rev.* 110, 6571–6594 (2010).
- 127. Abermann, S. Non-vacuum processed next generation thin film photovoltaics: Towards marketable efficiency and production of CZTS based solar cells. *Sol. Energy* **94**, 37–70 (2013).
- 128. Jiang, M. & Yan, X. Cu2ZnSnS4 thin film solar cells: present status and future prospects. Sol. Cells - Res. Appl. Perspect. 107–143 (2013) doi:http://dx.doi.org/10.5772/57353.
- 129. Yin, Y. & Alivisatos, A. P. Colloidal nanocrystal synthesis and the organic–inorganic interface. *Nature* **437**, 664–670 (2005).
- S., A., J., R. K. & S., M. B. Influence of co-ordinating and non-coordinating solvents in structural and morphological properties of Cu2ZnSnS4 (CZTS) nanoparticles. *Optik (Stuttg)*. 130, 99–105 (2017).
- Huang, T. J., Yin, X., Tang, C., Qi, G. & Gong, H. Influence of Ligands on the Formation of Kesterite Thin Films for Solar Cells: A Comparative Study. *ChemSusChem* 9, 1032–1041 (2016).
- 132. Zhang, X. *et al.* Efficient Thermolysis Route to Monodisperse Cu2ZnSnS4 Nanocrystals with Controlled Shape and Structure. *Sci. Rep.* **4**, 5086 (2015).
- Ataollahi, N. *et al.* Control of composition and grain growth in Cu 2 ZnSnS 4 thin films from nanoparticle inks. *Thin Solid Films* 674, 12–21 (2019).
- Hadke, S. H. *et al.* Synergistic Effects of Double Cation Substitution in Solution-Processed CZTS Solar Cells with over 10% Efficiency. *Adv. Energy Mater.* 8, 1–9 (2018).

- Datta, S. K. & Chaudhuri, A. K. On the mechanism of photoconductivity in polycrystalline lead selenide films. *Semicond. Sci. Technol.* 4, 376–381 (1989).
- Pal, U. Dark- and photoconductivity in doped and undoped zinc telluride films. *Semicond. Sci. Technol.* 8, 1331–1336 (1993).
- 137. Pal, R., Chattopadhyay, K. K., Chaudhuri, S. & Pal, A. K. Photoconductivity in CuInSe2 films. *Sol. Energy Mater. Sol. Cells* 33, 241–251 (1994).
- Kosyak, V., Karmarkar, M. A. & Scarpulla, M. A. Temperature dependent conductivity of polycrystalline Cu2ZnSnS4 thin films. *Appl. Phys. Lett.* 100, 263903 (2012).
- 139. Ghediya, P. R., Chaudhuri, T. K. & Vankhade, D. Electrical conduction of CZTS films in dark and under light from molecular solution ink. *J. Alloys Compd.* **685**, 498–506 (2016).
- González, J. C. *et al.* Hopping conduction and persistent photoconductivity in Cu2ZnSnS4 thin films. *J. Phys. D. Appl. Phys.* 46, 155107 (2013).
- 141. Moholkar, A. V. *et al.* Development of CZTS thin films solar cells by pulsed laser deposition: Influence of pulse repetition rate. *Sol. Energy* **85**, 1354–1363 (2011).
- 142. Park, H., Hwang, Y. H. & Bae, B. S. Sol-gel processed Cu2ZnSnS4 thin films for a photovoltaic absorber layer without sulfurization. *J. Sol-Gel Sci. Technol.* **65**, 23–27 (2013).
- 143. Muslih, E. Y. & Kim, K. H. Characteristics of Cu2ZnSnS4 thin film prepared by calcination and sulfurizing of metal (Cu,Zn,Sn)-ethanolamine precursor complexed from metal (Cu,Zn,Sn)-hydrate. *Chalcogenide Lett.* **12**, 349–355 (2015).
- 144. Deganello, D. Printing techniques for the fabrication of OLEDs. Organic Light-Emitting Diodes (OLEDs): Materials, Devices and Applications (Woodhead Publishing Limited, 2013). doi:10.1533/9780857098948.2.360.
- 145. Tsuda, A. & Venkata, N. K. The role of natural processes and surface energy of inhaled engineered nanoparticles on aggregation and corona formation. *NanoImpact* 2, 38–44 (2016).
- 146. Prasad, P. S. R. K., Reddy, A. V., Rajesh, P. K., Ponnambalam, P. & Prakasan, K. Studies on rheology of ceramic inks and spread of ink droplets for direct ceramic ink jet printing. J. Mater. Process. Technol. 176, 222–229 (2006).
- Soares, J. A. N. T. Introduction to Optical Characterization of Materials. in *Practical Materials Characterization* (ed. Sardela, M.) 43–92 (Springer-Verlag New York, 2014).

doi:10.1007/978-1-4614-9281-8.

- 148. Ingle, J. D. J. & Crouch, S. R. Spectrochemical analysis. (1988).
- 149. Akaltun, Y., Yildirim, M. A., Ateş, A. & Yildirim, M. The relationship between refractive index-energy gap and the film thickness effect on the characteristic parameters of CdSe thin films. *Opt. Commun.* **284**, 2307–2311 (2011).
- Li, W. *et al.* Recent Progress in Solution-Processed Copper-Chalcogenide Thin-Film Solar Cells. *Energy Technol.* 6, 46–59 (2018).
- 151. Yu, N. *et al.* Synthesis of Cu2ZnSnS4film by air-stable molecular-precursor ink for constructing thin film solar cells. *RSC Adv.* **4**, 36046–36052 (2014).
- Kim, H. T., Kim, D. & Park, C. Temperature effects on Cu 2ZnSnS 4 (CZTS) films deposited by spraying method. *Mol. Cryst. Liq. Cryst.* 564, 155–161 (2012).
- 153. Singh, S. *et al.* Selective Phase Transformation of Wurtzite Cu2ZnSn (SSe) 4 Nanocrystals into Zinc Blende and Kesterite by Solution and Solid State Transformations Selective Phase Transformation of Wurtzite Cu 2 ZnSn (SSe) 4 Nano- crystals into Zinc Blende and Kesteri. (2016) doi:10.1021/acs.chemmater.6b01845.
- Isotta, E., Pugno, N. M. & Scardi, P. Nanostructured kesterite (Cu2ZnSnS4) for applications in thermoelectric devices. *Powder Diffr.* 1–6 (2019) doi:10.1017/s0885715619000277.
- Kapusta, K. *et al.* From magnetic cubic pre-kesterite to semiconducting tetragonal kesterite Cu2ZnSnS4 nanopowders via the mechanochemically assisted route. *J. Alloys Compd.* 770, 981–988 (2019).
- Indubala, E., Sarveshvaran, S., Sudha, V., Mamajiwala, A. Y. & Harinipriya, S. Secondary phases and temperature effect on the synthesis and sulfurization of CZTS. *Sol. Energy* 173, 215– 224 (2018).
- 157. Williamson, G. . & Hall, W. . X-ray line broadening from filed aluminium and wolfram. *Acta Metall.* **1**, 22–31 (1953).
- 158. Scardi, P., Leoni, M., Delhez, R. & IUCr. Line broadening analysis using integral breadth methods: a critical review. *J. Appl. Crystallogr.* **37**, 381–390 (2004).
- Scardi, P. Chapter 13. Microstructural Properties: Lattice Defects and Domain Size Effects. in *Powder Diffraction* 376– 413 (Royal Society of Chemistry, 2008). doi:10.1039/9781847558237-00376.
- 160. Malerba, C. *et al.* CZTS stoichiometry effects on the band gap energy. *J. Alloys Compd.* **582**, 528–534 (2014).

- 161. Zhang, S. *et al.* Effect of different thermo-treatment at relatively low temperatures on the properties of indium-tin-oxide thin films. *Thin Solid Films* **636**, 702–709 (2017).
- Safdar, A. *et al.* Reaction Time and Film Thickness Effects on Phase Formation and Optical Properties of Solution Processed Cu2ZnSnS4 Thin Films. *J. Mater. Eng. Perform.* 25, 457–465 (2016).
- 163. Ghorpadea, U. V. *et al.* Wurtzite CZTS Nanocrystals and Phase Evolution to Kesterite Thin Film for Solar Energy Harvesting. *Phys. Chem. Chem. Phys.* 17, 19777–19788 (2015).
- Swami, S. K., Kumar, A. & Dutta, V. Deposition of kesterite Cu 2 ZnSnS 4 (CZTS) thin films by spin coating technique for solar cell application. *Energy Procedia* 33, 198–202 (2013).
- 165. Shin, S. W. *et al.* Studies on Cu2ZnSnS4 (CZTS) absorber layer using different stacking orders in precursor thin films. *Sol. Energy Mater. Sol. Cells* **95**, 3202–3206 (2011).
- 166. Muhunthan, N., Singh, O. P., Singh, S. & Singh, V. N. Growth of CZTS thin films by co-sputtering of metal targets and sulfurization in H 2 S N. Muhunthan, Om Pal Singh, Son Singh, and V.N. Singh* CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi-110012. *Int. J. Photoenergy* 2013, 1–23 (2013).
- 167. Bard, A. J. & Faulkner, L. R. *Electrochemical methods : fundamentals and applications*. (Wiley, 2001).
- 168. Yue, G. *et al.* A highly efficient flexible dye-sensitized solar cell based on nickel sulfide/platinum/titanium counter electrode. *Nanoscale Res. Lett.* **10**, 1 (2015).
- Larcher, D. & Tarascon, J.-M. Towards greener and more sustainable batteries for electrical energy storage. *Nat. Chem.* 7, 19–29 (2015).
- 170. Bagher, A. M. Introduction to Organic Solar Cells. *Sustain. Energy* **2**, 85–90 (2014).
- Ahmad, S., Guillén, E., Kavan, L., Grätzel, M. & Nazeeruddin, M. K. Metal free sensitizer and catalyst for dye sensitized solar cells. *Energy Environ. Sci.* 6, 3439–3466 (2013).
- 172. Rao, S., Morankar, A., Verma, H. & Goswami, P. Emerging Photovoltaics : Organic , Copper Zinc Tin Sulphide and Perovskite-based Solar Cells. J. Appl. Chem. **2016**, 1–20 (2016).
- Wang, H. & Hu, Y. H. Graphene as a counter electrode material for dye-sensitized solar cells. *Energy Environ. Sci.* 5, 8182 (2012).
- 174. Li, Z. et al. Environmentally friendly solution route to kesterite

Cu2ZnSn(S,Se)4 thin films for solar cell applications. *RSC Adv.* **4**, 26888–26894 (2014).

- Marchionna, S. *et al.* Cu2ZnSnS4 solar cells grown by sulphurisation of sputtered metal precursors. *Thin Solid Films* 542, 114–118 (2013).
- Goetzberger, A., Hebling, C. & Schock, H.-W. Photovoltaic materials, history, status and outlook. *Mater. Sci. Eng. R Reports* 40, 1–46 (2003).
- 177. Kim, H.-S. *et al.* Lead iodide perovskite sensitized all-solidstate submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Sci. Rep.* **2**, 591 (2012).
- Navrotsky, A. Energetics and Crystal Chemical Systematics among Ilmenite, Lithium Niobate, and Perovskite Structures. (1998) doi:10.1021/CM9801901.
- Bao, N. & Gupta, A. Inorganic Spintronic Materials. *Encycl. Inorg. Bioinorg. Chem.* 1–15 (2013) doi:10.1002/9781119951438.eibc2159.
- Metalgrass LTD. Perovskite introduction. *Metalgrass LTD* https://www.perovskite-info.com/perovskite-introduction (2018).
- 181. Chaudhary, D. K., Kumar, P. & Kumar, L. Realization of efficient perovskite solar cells with MEH : PPV hole transport layer. J. Mater. Sci. Mater. Electron. 1–7 (2016) doi:10.1007/s10854-016-5942-y.
- 182. Rhee, J. H., Chung, C. & Diau, E. W. REVIEW A perspective of mesoscopic solar cells based on metal chalcogenide quantum dots and organometal-halide perovskites. *NPG Asia Mater.* 5, e68-17 (2013).
- Wong, M. K. *et al.* Synthesis of Lead-Free Perovskite Films by Combinatorial Evaporation: Fast Processes for Screening Different Precursor Combinations. *Chem. Mater.* 29, 9946– 9953 (2017).
- 184. Zhang, J. *et al.* n-Type Doping and Energy States Tuning in CH 3 NH 3 Pb 1– x Sb 2 x /3 I 3 Perovskite Solar Cells. ACS Energy Letters 535–541 (2016) doi:10.1021/acsenergylett.6b00241.
- 185. Stranks, S. D. *et al.* Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science* 342, 341–4 (2013).
- Mailoa, J. P. *et al.* A 2-terminal perovskite/silicon multijunction solar cell enabled by a silicon tunnel junction. *Appl. Phys. Lett.* **106**, (2015).
- 187. Werner, J. *et al.* Efficient Monolithic Perovskite/Silicon Tandem Solar Cell with Cell Area >1 cm2. *J. Phys. Chem.*

Lett. 3-8 (2016) doi:10.1021/acs.jpclett.5b02686.

- Lee, M. M., Teuscher, J., Miyasaka, T., Murakami, T. N. & Snaith, H. J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science (80-.*). 338, 643 (2012).
- Pascoe, A. R. *et al.* Planar versus mesoscopic perovskite microstructures: The influence of CH3NH3PbI3morphology on charge transport and recombination dynamics. *Nano Energy* 22, 439–452 (2016).
- 190. Snaith, H. J. *et al.* Anomalous Hysteresis in Perovskite Solar Cells. *J. Phys. Chem. Lett.* **5**, 1511–1515 (2014).
- 191. Xing, G. *et al.* Long-range balanced electron-and holetransport lengths in organic-inorganic CH3NH3PbI3. *Science* (80-.). **342**, 344–347 (2013).
- 192. Xu, J. *et al.* Perovskite–fullerene hybrid materials suppress hysteresis in planar diodes. *Nat. Commun.* **6**, 7081 (2015).
- Luo, W. *et al.* Dopant-free Spiro-OMeTAD as hole transporting layer for stable and efficient perovskite solar cells. *Org. Electron.* 74, 7–12 (2019).
- 194. Hu, L. *et al.* PEDOT:PSS monolayers to enhance the hole extraction and stability of perovskite solar cells. *J. Mater. Chem. A* 6, 16583–16589 (2018).
- 195. Tian, H., Xu, B., Chen, H., Johansson, E. M. J. & Boschloo, G. Solid-state perovskite-sensitized p-type mesoporous nickel oxide solar cells. *ChemSusChem* 7, 2150–2153 (2014).
- 196. Yu, W. *et al.* Ultrathin Cu 2 O as an efficient inorganic hole transporting material for perovskite solar cells. *Nanoscale* 8, 6173–6179 (2016).
- 197. Ge, J., Grice, C. R. & Yan, Y. Cu-based quaternary chalcogenide Cu ₂ BaSnS ₄ thin films acting as hole transport layers in inverted perovskite CH ₃ NH ₃ PbI ₃ solar cells. *J. Mater. Chem. A* 5, 2920–2928 (2017).
- 198. Yang, D. *et al.* Stable Efficiency Exceeding 20.6% for Inverted Perovskite Solar Cells through Polymer-Optimized PCBM Electron-Transport Layers. *Nano Lett.* 19, 3313–3320 (2019).
- 199. Li, Y. *et al.* High performance planar-heterojunction perovskite solar cells using amino-based fulleropyrrolidine as the electron transporting material. *J. Mater. Chem. A* **4**, 10130–10134 (2016).
- 200. Sun, C. *et al.* Amino-Functionalized Conjugated Polymer as an Efficient Electron Transport Layer for High-Performance Planar-Heterojunction Perovskite Solar Cells. *Adv. Energy Mater.* 6, 1–10 (2016).
- 201. Wojciechowski, K., Saliba, M., Leijtens, T., Abate, A. &

Snaith, H. J. Sub 150 °C Processed Meso-superstructured Perovskite Solar Cells with Enhanced Efficiency Konrad. *Energy Environ. Sci.* **7**, 1142–1147 (2014).

- 202. Ma, J. *et al.* Low-Temperature Solution-Processed ZnO Electron Transport Layer for Highly Efficient and Stable Planar Perovskite Solar Cells with Efficiency Over 20%. *Sol. RRL* 3, 1900096 (2019).
- 203. Li, X. *et al.* Low-Temperature Solution-Processed ZnSe Electron Transport Layer for Efficient Planar Perovskite Solar Cells with Negligible Hysteresis and Improved Photostability. *ACS Nano* 12, 5605–5614 (2018).
- 204. Isotta, Fanciulli, Pugno & Scardi. Effect of the Order-Disorder Transition on the Seebeck Coefficient of Nanostructured Thermoelectric Cu2ZnSnS4. *Nanomaterials* **9**, 762 (2019).
- 205. Christians, J. A., Fung, R. C. M., Kamat, P. V & Accepted, J. An Inorganic Hole Conductor for Organo-Lead Halide Perovskite Solar Cells . Improved Hole Conductivity with Copper Iodide. (2013).
- Dualeh, A. *et al.* Impedance Spectroscopic Analysis of Lead Iodide Perovskite-Sensitized Solid-State Solar Cells. *ACS Nano* 8, 362–373 (2014).
- 207. Yuan, M. *et al.* Controlling the Band Gap to Improve Open-Circuit Voltage in Metal Chalcogenide based Perovskite Solar Cells. *Electrochim. Acta* 215, 374–379 (2016).
- 208. Riha, S. C., Parkinson, B. A. & Prieto, A. L. Compositionally Tunable Cu ₂ ZnSn(S _{1-x} Se _x) 4 Nanocrystals: Probing the Effect of Se-Inclusion in Mixed Chalcogenide Thin Films. J. Am. Chem. Soc. 133, 15272–15275 (2011).
- 209. G. Schlichthörl, S. Y. Huang, J. Sprague, and & Frank*, A. J. Band Edge Movement and Recombination Kinetics in Dye-Sensitized Nanocrystalline TiO2 Solar Cells: A Study by Intensity Modulated Photovoltage Spectroscopy. (1997) doi:10.1021/JP9714126.
- Steinhagen, C. *et al.* Synthesis of Cu₂ZnSnS₄ Nanocrystals for Use in Low-Cost Photovoltaics. *J. Am. Chem. Soc.* 131, 12554–12555 (2009).
- Rosen, E. L. *et al.* Exceptionally Mild Reactive Stripping of Native Ligands from Nanocrystal Surfaces by Using Meerwein's Salt. *Angew. Chemie Int. Ed.* 51, 684–689 (2012).
- 212. Saliba, M. *et al.* Influence of Thermal Processing Protocol upon the Crystallization and Photovoltaic Performance of Organic–Inorganic Lead Trihalide Perovskites. *J. Phys. Chem. C* 118, 17171–17177 (2014).
- 213. Sun, K. et al. Over 9% Efficient Kesterite Cu 2 ZnSnS 4 Solar
Cell Fabricated by Using Zn $_{1-x}$ Cd $_x$ S Buffer Layer. *Adv. Energy Mater.* **6**, 1600046 (2016).

- 214. Fallahazad, P., Naderi, N., Eshraghi, M. J. & Massoudi, A. Combination of surface texturing and nanostructure coating for reduction of light reflection in ZnO/Si heterojunction thin film solar cell. J. Mater. Sci. Mater. Electron. 29, 6289–6296 (2018).
- Zekry, Z. & Eldallal, G. Effect of MS contact on the electrical behaviour of solar cells. *Solid. State. Electron.* **31**, 91–97 (1988).
- 216. Chaudhari, S., P.K., K. & Dey, S. R. Investigation of optimum annealing parameters for formation of dip coated Cu2ZnSnS4 thin film. *Thin Solid Films* **612**, 456–462 (2016).
- 217. Khattak, Y. H., Baig, F., Toura, H., Beg, S. & Soucase, B. M. CZTSe Kesterite as an Alternative Hole Transport Layer for MASnI3 Perovskite Solar Cells. *J. Electron. Mater.* 48, 5723–5733 (2019).
- 218. Vanalakar, S. A. *et al.* Effect of post-annealing atmosphere on the grain-size and surface morphological properties of pulsed laser deposited CZTS thin films. *Ceram. Int.* **40**, 15097–15103 (2014).
- Ataollahi, N. *et al.* Synthesis and Post-Annealing of Cu 2 ZnSnS 4 Absorber Layers Based on Oleylamine / 1dodecanethiol. *Materials (Basel).* 12, 14 (2019).
- 220. Tiwari, D. *et al.* Impact of Sb and Na Doping on the Surface Electronic Landscape of Cu ₂ ZnSnS ₄ Thin Films. *ACS Energy Lett.* **3**, 2977–2982 (2018).
- 221. Scragg, J. J. S., Choubrac, L., Lafond, A., Ericson, T. & Platzer-Björkman, C. A low-temperature order-disorder transition in Cu2ZnSnS4 thin films. *Appl. Phys. Lett.* **104**, 2–6 (2014).
- 222. Scragg, J. J. S. *et al.* Cu-Zn disorder and band gap fluctuations in Cu2ZnSn(S,Se)4: Theoretical and experimental investigations. *Phys. Status Solidi Basic Res.* 253, 247–254 (2016).
- 223. Valentini, M. *et al.* Effect of the order-disorder transition on the optical properties of Cu2ZnSnS4. *Appl. Phys. Lett.* **108**, 211909 (2016).
- 224. Rey, G. *et al.* On the origin of band-tails in kesterite. in *Solar Energy Materials and Solar Cells* vol. 179 142–151 (Elsevier B.V., 2018).
- 225. Lang, M. *et al.* Impact of the degree of Cu-Zn order in Cu2ZnSn(S,Se)4 solar cell absorbers on defect states and band tails. *Appl. Phys. Lett.* **113**, 033901 (2018).

- 226. Larsen, J. K., Scragg, J. J. S., Ross, N. & Platzer-Björkman, C. Band Tails and Cu-Zn Disorder in Cu2ZnSnS4Solar Cells. ACS Appl. Energy Mater. 3, 7520–7526 (2020).
- 227. Liu, M. L., Huang, F. Q., Chen, L. D. & Chen, I. W. A wideband-gap p -type thermoelectric material based on quaternary chalcogenides of Cu2ZnSnQ4 (Q=S,Se). *Appl. Phys. Lett.* 94, 3–6 (2009).
- 228. Yang, H., Jauregui, L. A., Zhang, G., Chen, Y. P. & Wu, Y. Nontoxic and abundant copper zinc tin sulfide nanocrystals for potential high-temperature thermoelectric energy harvesting. *Nano Lett.* **12**, 540–545 (2012).
- 229. Isotta, E., Mukherjee, B., Fanciulli, C., Pugno, N. M. & Scardi, P. Order-Disorder Transition in Kesterite Cu2ZnSnS4: Thermopower Enhancement via Electronic Band Structure Modification. J. Phys. Chem. C 124, 7091–7096 (2020).
- Jiang, Q. *et al.* Colossal thermoelectric enhancement in Cu2+xZn1-xSnS4solid solution by local disordering of crystal lattice and multi-scale defect engineering. *J. Mater. Chem. A* 8, 10909–10916 (2020).
- 231. Gunavathy, K. V., Tamilarasan, K., Rangasami, C. & Arulanantham, A. M. S. Solution processed copper zinc tin sulfide thin films for thermoelectric device applications. *Ceram. Int.* 46, 28342–28354 (2020).
- Zeng, Y. *et al.* The structural, optical and thermoelectric properties of single target sputtered Cu2ZnSn(S,Se)4 thin film. *J. Mater. Sci. Mater. Electron.* 28, 13763–13769 (2017).
- 233. Ashfaq, A. *et al.* Tailoring the thermoelectric properties of solgel grown CZTS/ITO thin films by controlling the secondary phases. *Phys. B Condens. Matter* **558**, 86–90 (2019).
- 234. Burton, M. R. *et al.* Thin Film Tin Selenide (SnSe) Thermoelectric Generators Exhibiting Ultralow Thermal Conductivity. *Adv. Mater.* **30**, 1801357 (2018).
- Talin, A. A. *et al.* Tunable electrical conductivity in metalorganic framework thin-film devices. *Science (80-.).* 343, 66– 69 (2014).
- 236. Ilami, M. *et al.* Magnetically Actuated Tunable Soft Electronics. *ACS Omega* **4**, 21242–21250 (2019).
- 237. Heine, T. Transition metal chalcogenides: Ultrathin inorganic materials with tunable electronic properties. *Acc. Chem. Res.* 48, 65–72 (2015).
- 238. Liu, Y. *et al.* Ultrathin MEMS thermoelectric generator with Bi2Te3/(Pt, Au) multilayers and Sb2Te3 legs. *Nano Converg.* 7, 1–11 (2020).
- 239. Snyder, G. J., Lim, J. R., Huang, C. K. & Fleurial, J. P.

Thermoelectric microdevice fabricated by a MEMS-like electrochemical process. *Nat. Mater.* **2**, 528–531 (2003).

- 240. Zhang, Z. & Ma, Y. DC-25 GHz and low-loss MEMS thermoelectric power sensors with floating thermal slug and reliable back cavity based on GaAs MMIC technology. *Micromachines* 9, (2018).
- 241. Gould, C. & Shammas, N. A Review of Thermoelectric MEMS Devices for Micro-power Generation, Heating and Cooling Applications. in *Micro Electronic and Mechanical Systems* (ed. Takahata, K.) (InTech, 2009). doi:10.5772/7001.
- 242. Energy Harvesting Technologies. Springer (Springer Science+Business Media, LLC, 2009). doi:10.1007/978-0-387-76464-1.
- Hicks, L. D. & Dresselhaus, M. S. Effect of quantum-well structures on the thermoelectric figure of merit. *Phys. Rev. B* 47, 12727–12731 (1993).
- 244. Venkatasubramanian, R., Siivola, E., Colpitts, T. & O'Quinn, B. Thin-film thermoelectric devices with high room-temperature figures of merit. *Nature* 413, 597–602 (2001).
- 245. Dresselhaus, M. S. *et al.* New directions for low-dimensional thermoelectric materials. *Adv. Mater.* **19**, 1043–1053 (2007).
- 246. Chen, X., Zhou, Z., Lin, Y. H. & Nan, C. Thermoelectric thin films: Promising strategies and related mechanism on boosting energy conversion performance. *J. Mater.* **6**, 494–512 (2020).
- 247. Scardi, P. & Leoni, M. Whole powder pattern modelling. *Acta Crystallogr. Sect. A Found. Crystallogr.* 58, 190–200 (2002).
- 248. Scardi, P., Azanza Ricardo, C. L., Perez-Demydenko, C. & Coelho, A. A. Whole powder pattern modelling macros for TOPAS. *J. Appl. Crystallogr.* **51**, 1752–1765 (2018).
- 249. Leoni, M., Confente, T. & Scardi, P. PM2K: A flexible program implementing Whole Powder Pattern Modelling. in *Zeitschrift fur Kristallographie, Supplement* vol. 1 249–254 (R. Oldenbourg Verlag GmbH, 2006).
- 250. Isotta, E. Nanostructured thermoelectric kesterite Cu2ZnSnS4. (University of Trento, 2021).
- 251. Linseis, V., Völklein, F., Reith, H., Nielsch, K. & Woias, P. Advanced platform for the in-plane ZT measurement of thin films. *Rev. Sci. Instrum.* **89**, 015110 (2018).
- 252. Liu, T. *et al.* Enhanced control of self-doping in halide perovskites for improved thermoelectric performance. *Nat. Commun.* **10**, 1–9 (2019).
- 253. Liu, T. *et al.* Unusual Thermal Boundary Resistance in Halide Perovskites: A Way to Tune Ultralow Thermal Conductivity for Thermoelectrics. *ACS Appl. Mater. Interfaces* **11**, 47507–

47515 (2019).

- 254. Lafond, A., Choubrac, L., Guillot-Deudon, C., Deniard, P. & Jobic, S. Crystal structures of photovoltaic chalcogenides, an intricate puzzle to solve: The cases of CIGSe and CZTS materials. *Zeitschrift fur Anorg. und Allg. Chemie* **638**, 2571–2577 (2012).
- 255. Andreas Leineweber, Robert Dinnebier & John S. O. Evans. *Rietveld Refinement. Rietveld Refinement* (De Gruyter STEM, 2018). doi:10.1515/9783110461381.
- 256. Pei, Y. *et al.* Convergence of electronic bands for high performance bulk thermoelectrics. *Nature* **473**, 66–69 (2011).
- 257. Zeier, W. G. *et al.* Band convergence in the non-cubic chalcopyrite compounds Cu2MGeSe4. *J. Mater. Chem. C* **2**, 10189–10194 (2014).
- 258. Scragg, J. J. S. *et al.* Cu-Zn disorder and band gap fluctuations in Cu ₂ ZnSn(S,Se) ₄: Theoretical and experimental investigations. *Phys. status solidi* **253**, 247–254 (2016).
- 259. Rudisch, K., Ren, Y., Platzer-Björkman, C. & Scragg, J. Order-disorder transition in B-type Cu2ZnSnS4 and limitations of ordering through thermal treatments. *Appl. Phys. Lett.* 108, (2016).
- 260. Trinh, T. Q., Nguyen, T. T., Vu, D. V. & Le, D. H. Structural and thermoelectric properties of Al-doped ZnO thin films grown by chemical and physical methods. *J. Mater. Sci. Mater. Electron.* **28**, 236–240 (2017).
- Chen, T. H., Cheng, T. C. & Hu, Z. R. The electrical and optical properties of AZO thin film under different postannealing temperatures. *Microsyst. Technol.* 19, 1787–1790 (2013).
- 262. Ohtaki, M., Tsubota, T., Eguchi, K. & Arai, H. Hightemperature thermoelectric properties of (Zn1-xAlx)O. J. Appl. Phys. 79, 1816–1818 (1996).
- Tsubota, T., Ohtaki, M., Eguchi, K. & Arai, H. Thermoelectric properties of Al-doped ZnO as a promising oxide material for high-temperature thermoelectric conversion. *J. Mater. Chem.* 7, 85–90 (1997).
- 264. Ma, N. *et al.* Microstructure and thermoelectric properties of Zn1-xAlxO ceramics fabricated by spark plasma sintering. *J. Phys. Chem. Solids* **71**, 1344–1349 (2010).
- 265. Jood, P. *et al.* Al-doped zinc oxide nanocomposites with enhanced thermoelectric properties. *Nano Lett.* **11**, 4337–4342 (2011).
- 266. Jantrasee, S., Moontragoon, P. & Pinitsoontorn, S. Thermoelectric properties of Al-doped ZnO: Experiment and

simulation. J. Semicond. 37, (2016).

- 267. Xu, Y., Goto, M., Kato, R., Tanaka, Y. & Kagawa, Y. Thermal conductivity of ZnO thin film produced by reactive sputtering. *J. Appl. Phys.* **111**, (2012).
- 268. Loureiro, J. *et al.* Transparent aluminium zinc oxide thin films with enhanced thermoelectric properties. *J. Mater. Chem. A* **2**, 6649–6655 (2014).
- 269. Tanner, D. B. & Larson, D. C. Electrical resistivity of silver films. *Phys. Rev.* **166**, 652–655 (1968).
- 270. De Vries, J. W. C. Temperature and thickness dependence of the resistivity of thin polycrystalline aluminium, cobalt, nickel, palladium, silver and gold films. *Thin Solid Films* **167**, 25–32 (1988).
- 271. Park, N. W. *et al.* Control of phonon transport by the formation of the Al2O3 interlayer in Al2O3-ZnO superlattice thin films and their in-plane thermoelectric energy generator performance. *Nanoscale* **9**, 7027–7036 (2017).
- 272. Chen, T., Zheng, Z., Liang, G. & Fan, P. A new design of a thin-film thermoelectric device based on multilayer-structure module. *Nanomaterials* **10**, (2020).
- 273. Song, X. *et al.* A review on development prospect of CZTS based thin film solar cells. *Int. J. Photoenergy* **2014**, (2014).
- Chen, L. & Park, C. Effects of annealing temperature on Cu2ZnSnS4 (CZTS) films formed by electrospray technique. *Korean J. Chem. Eng.* 34, 1187–1191 (2017).
- 275. Zhou, A. *et al.* Impact of the film thickness and substrate on the thermopower measurement of thermoelectric films by the potential-Seebeck microprobe (PSM). *Appl. Therm. Eng.* **107**, 552–559 (2016).
- Min, G. & Rowe, D. M. Cooling performance of integrated thermoelectric microcooler. *Solid. State. Electron.* 43, 923–929 (1999).

Credits of the cover image:

Eleonora Isotta, University of Trento Tina Casey, CleanTechnica.com



Contents on this book are licensed under a Creative Common Attribution Non Commercial - No Derivatives 4.0 International License, except for the parts already published by other publishers.

University of Trento Doctoral School in Civil, Environmental and Mechanical Engineering *http://web.unitn.it/en/dricam* Via Mesiano 77, I-38123 Trento Tel. +39 0461 282670 / 2611 - *dicamphd@unitn.it* The search for renewable energy resources and ways to harvest them has become a global mainstream topic among researchers nowadays, with solar cells and thermoelectric generators among the energy harvesting technologies currently being researched in vast. CZTS (Cu2ZnSnS4), a p-type semiconducting material initially researched to replace copper indium gallium selenide (CIGS) as the light absorbing layer in thin film solar cells, was studied in this doctoral work for alternative uses in energy harvesting. This work aims to systemically investigate the prospects of CZTS to be used as hole transport layers and thermoelectric generators.

CZTS thin film was successfully fabricated using a versatile approach involving hot-injection synthesis of CZTS nanoparticles ink followed by spin coating and thermal treatment. Results obtained revealed the possibility to fine control CZTS thin film fabrication based on ink concentration and spin. Besides that, thermal treatment temperature was found to affect the film's overall properties, where an increase in thermal treatment temperature improved the degree of crystallinity and electrical properties. In addition, a phase change going from less stable cubic and wurtzite structures to a more stable tetragonal structure was also observed. Furthermore, CZTS was found to be a good candidate to replace the commonly used organic hole transport layer in perovskite solar cells, with potentials in improving performance and stability. In addition, CZTS also possessed good transport properties to be a potential p-type material in a thermoelectric generator, with the preliminary performance of fabricated CZTS/AZO thermoelectric generator showing a maximum power output of ~350 nW at ~170 K ΔT.

These findings provide new perspectives for CZTS in energy harvesting applications, despite the struggle in its development as the absorber layer in thin film solar cells. Besides providing a deeper understanding of CZTS and its vast possibilities in energy harvesting applications, promising future research stemming from this work is also limitless, reinventing ways in material studies, in search of alternative applications which may be of benefit.

Muhammad Ubaidah Syafiq bin Mustaffa was born on 30th April 1993 in Kuala Lumpur, Malaysia. He is the first child of Mustaffa bin Musa and Yusliza binti Yusoff, out of six. He did his undergraduate study in Chemical Technology at the National University of Malaysia and graduated in 2015 with CGPA of 3.70. During his undergraduate study, he went for an internship at a glove-making factory (Ansell Ltd.), focusing on manufacturing processes in industrial scale. He then continued his master's study in Energy Technology at the same university and graduated in 2017 with CGPA of 3.86. He then got accepted to be a researcher at the Solar Energy Research Institute, the National University of Malaysia, and currently on study leave to pursue his PhD study. On the 11th of December 2018, he got married to Raja Nur Haziqah bt Raja Zulkarnain. As of now, he is currently enrolled since November 2017 in the Department of Civil, Environmental, and Mechanical Engineering at the University of Trento, Italy for his PhD study in materials for renewable energy generation.