EFFECT OF SYNTHESIS TEMPERATURE ON PHOTOCONVERSION EFFICIENCY OF DOUBLE PEROVSKITE Cs₂AgBiBr₆ SOLAR CELLS

MTech. Thesis

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INDIAN INSTITUTE OF TECHNOLOGY INDORE

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EFFECT OF SYNTHESIS TEMPERATURE ON PHOTOCONVERSION EFFICIENCY OF DOUBLE PEROVSKITE Cs₂AgBiBr₆ SOLAR CELLS

A THESIS

Submitted in partial fulfillment of the Requirements for the award of the degree of Master of Technology

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled 'EFFECT OF SYNTHESIS TEMPERATURE ON THE PHOTOCONVERSION EFFICIENCY OF DOUBLE PEROVSKITE Cs₂AgBiBr₆ SOLAR CELLS' in the partial fulfillment of the requirements for the award of the degree of MASTER OF TECHNOLOGY and submitted in the DISCIPLINE OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from August 2023, II year M.Tech. to June 2024 II year of M.Tech. Thesis submission under the supervision of Dr. Parasharam M. Shirage, Professor, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date (SHAIKH AZAHARUDDIN SALEEM)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of the Supervisor of M.Tech. thesis #1 (with date) (PROF. PARASHARAM M. SHIRAGE)

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DEDICATION

Dedicated to

My Mother

ABSTRACT

Perovskite solar cells, a prominent subset within the third generation of solar cells, have garnered considerable attention within the realm of emerging photovoltaic technologies. They have achieved notable power conversion efficiencies (PCE) exceeding 24%, outperforming several counterparts among third-generation solar cells. They are widely regarded as the most promising successors to conventional silicon solar cells. Despite their commendable photophysical attributes, lead halide perovskites face significant challenges, particularly concerning stability and the toxicity associated with lead. As a response, there has been a concerted effort towards researching lead-free halide perovskites (LFHP) with improved stability. In this study, a electron transport layer (ETL) TiO₂ film is synthesized, and its structural, morphological, optical, and photoelectrochemical properties are thoroughly investigated to assess its potential utility in LFHP solar cells. Notably, the synthesis of phase pure Cs₂AgBiBr₆ and its integration into thin films for solar cell fabrication have been focal points in prior research endeavors. This study demonstrates a straightforward spin-coating method for synthesizing Cs₂AgBiBr₆ under ambient conditions. Furthermore, it was observed that post-spin-coating heat treatment influences the grain size of the film, thereby directly impacting the photoconversion efficiency of the device. Efforts to reduce the cost of the current hole transport layer (HTL) while simultaneously enhancing performance have been a focal point of research. In this study, CuSCN is employed as the HTL without compromising performance. Comprehensive physicochemical characterizations using techniques such as FESEM, XRD, UV-Vis spectroscopy, XPS, and Raman spectroscopy were conducted on the produced films. The photovoltaic investigations revealed a significant improvement in photoelectrochemical performance attributed to larger grain sizes. Additionally, this study explores the functionalities of various low-cost and environmentally friendly counter electrodes. The resulting solar cells exhibited an exceptional conversion efficiency of 1.75%.

Key words: Lead-free solar cell, TiO₂, Spin Coating, Cs₂AgBiBr₆, Copper thiocyanate.

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Abbreviations

Power conversion efficiency	PCE
Lead-free halide perovskites	LFHP
Hole transport layer	HTL
Photovoltaic	PV
Cadmium telluride	CdTe
Copper indium gallium di-selenide	CIGS
Dye-sensitized solar cells	DSSCs
Perovskite solar cells	PSCs
Lead	Pb
Photoluminescence	PL
Open circuit voltage	V _{OC}
Short circuit current	\mathbf{J}_{SC}
Fill factor	FF
Fluorine doped tin oxide	FTO
Deionised water	DI
Dimethyl sulfoxide	DMSO
Polyvinyl pyrrolidone	PVP
Titanium (IV) isopropoxide	TTIP
X-ray diffraction	XRD
Field-emission scanning electron microscopy	FESEM
X-ray photoelectron spectroscopy	XPS
Atomic force microscopy	AFM

Transmission electron microscopy	
Current density-voltage	J-V
Average roughness	Ra
Root mean square roughness	Rq
Electron spectroscopy for chemical analysis	ESCA
Highest occupied molecular orbital	НОМО
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Valence band	VB
Conduction band	CB

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Chapter 1

Introduction and Literature Review

1. Introduction

1.1. What are Solar cells?

Solar energy refers to the tremendous quantity of energy that the sun produces every day in the form of heat and radiation. It is a cost-free, infinitely renewable source of energy. The primary advantage of solar energy among other conventional power sources is that it can be generated entirely from sunlight using photovoltaic (PV) solar cells. The sun, a massive, hot glowing ball of helium and hydrogen gas, produces energy through the nuclear fusion of hydrogen nuclei at its core, forming helium and energy. This process shown in **Figure 1.1** results in a vast, sphere-shaped gaseous mass primarily composed of hydrogen nuclei undergoing fusion.



Figure 1.1 Schematics of the nuclear fusion process which led to the production of solar energy [1].

In 2022, the global renewable energy sector saw significant growth, with renewable generation capacity reaching 3,372 GW. This expansion was driven by solar and wind energy, which together contributed 90% of the net renewable additions. Solar power saw a remarkable increase of 192 GW, while wind power added 75 GW. Asia, led by China, was at the forefront of this capacity expansion, with notable increases also seen in Europe and North America. The rise of renewables was further underscored by their share in total capacity expansion, which reached 83% in 2022, indicating a growing dominance of renewable energy sources in the global energy landscape as shown in **Figure 1.2**.



Figure 1.2 Yearly Global Energy Generation Capacity of different Renewable energy resources estimated in 2022 and total capacity added in 2022 alone [2].

The historical journey of solar cells is a testament to humanity enduring fascination with harnessing solar power. Millennia ago, our ancestors used solar energy for practical purposes like igniting fires and providing light. Scientific exploration of solar energy began in earnest in the 18th century with scholars such as John Herschel, Samuel Pierpont Langley, and Horace de Saussure who sought to understand its potential applications. However, it wasn't until 1839 [3], when Edmond Becquerel discovered the PV effect, that the possibility of directly converting sunlight into electricity was realized. This breakthrough laid the groundwork for Charles Fritts' development of solid-state PV cell in 1883 for the first time [4]. Albert Einstein's work on the photoelectric effect in 1905 provided a theoretical framework for understanding the behavior of light and electrons, further propelling research in solar energy conversion [5]. The mid-20th century saw significant advancements, culminating in the creation of the first modern siliconbased PV cell by Calvin Fuller, Gerald Pearson, and Daryl Chapin at Bell Laboratories in the 950s [6]. Initially utilized for space exploration, these early solar cells paved the way for practical applications on Earth. The 1970s marked a turning point with Elliot Berman's work at Exxon, which significantly reduced the cost of silicon solar cells, making them economically viable for widespread use [7]. This development catalyzed the proliferation of solar panels in residential and commercial settings, laying the foundation for the renewable energy revolution. In recent years, research has shifted towards exploring alternative materials and advanced cell designs to further enhance efficiency and affordability. Technologies such as organic PVs, III-V semiconductors, thin-film solar cells, perovskites, quantum dots, and carbon nanotubes hold the promise of pushing the boundaries of solar energy conversion beyond the limitations of traditional silicon-based cells.

1.2. Types of solar cells

Based on their performance and requirements, solar cells are broadly divided into three categories. **Figure 1.3** represents the categories of solar cells.



Figure 1.3 Types of solar cells [8].

1.2.1. First-Generation Solar Cells

First-generation solar cells are primarily based on crystalline silicon, either monocrystalline or polycrystalline. These cells have dominated the market due to their high efficiency, affordability, and long-term stability. Monocrystalline silicon cells, made from a single continuous crystal structure, offer efficiencies of up to 27% [9-12]. Polycrystalline silicon cells, made from silicon crystals melted together, are slightly less efficient but cheaper to produce. Band gap energy of 1.12 eV for silicon solar cell, which aligns well with the solar spectrum. Techniques such as surface texturing and antireflection coatings enhance light absorption even in thin wafers. These cells represent a significant portion of global solar cell production.

1.2.2. Second Generation Solar Cells

Second-generation solar cells, such as a-Si amorphous silicon, and thin-film cells like cadmium telluride (CdTe) and copper indium gallium di-selenide (CIGS), offer economical alternatives to traditional silicon wafer cells [13]. Thin-film technology, with layers as thin as 1 μ m compared to the 350 μ m layers in silicon-wafer cells, significantly reduces material and production costs. Amorphous silicon cells, made at low processing temperatures on inexpensive, flexible substrates like polymers, are ideal for mass production on various surfaces. Despite lower efficiency (4%-8%), a-Si cells are cost-effective and versatile for low-power devices [14]. CdTe and CIGS cells, achieving over 20% efficiency this year, are promising for commercial PV applications [15]. However, the toxicity of cadmium in CdTe cells and material scarcity in both CdTe and CIGS cells require sustainable manufacturing and disposal methods. Challenges such as stability issues and competition from crystalline silicon technologies hinder widespread adoption. Continued research and innovation are crucial to enhancing the sustainability and market practicality of thin-film solar cells.

1.2.3. Third generation solar cells

A paradigm shift in PV technology is caused by emergence of third generation solar cells, moving beyond traditional silicon-based methods to explore novel materials and designs. These advanced cells include nanocrystal-based, polymer-based, dve-sensitized. concentrated, and perovskite-based varieties, utilizing materials such as nanotubes, organic dyes, conductive polymers, quantum dots, and perovskites. While lab efficiencies range from 3% to over 25%, commercialization remains challenging [16-18]. Polymer solar cells are flexible and scalable but face stability issues. Perovskite-based cells have achieved record efficiencies but struggle with toxicity and longterm stability. Among emerging technologies, dye-sensitized solar cells (DSSCs) and perovskite solar cells (PSCs) are notable. DSSCs, introduced by Gratzel and O'Regan in 1991 [19]. use titanium dioxide nanoparticles and molecular dyes to mimic photosynthesis. Despite their breakthrough, DSSCs are still under development, with research focusing on efficiency and stability improvements, such as co-doping with quantum dots and using solid-state electrolytes. PSCs, based on ABX₃ perovskite crystal structures, offer high charge carrier mobility,

broad optical absorption, and cost-effective manufacturing. The comparison of historical values with projected targets for the cost of electricity in solar power is shown in **Figure 1.4**. Their efficiency surged from 3.8% in 2009 to 25.2% in 2020 *[20]*. highlighting their rapid advancement. However, issues like environmental stability and scalable production remain, requiring ongoing R&D.

Despite the complexities, third-generation solar cells are pivotal for more efficient, sustainable, and accessible solar energy. Continued innovation is essential to overcome technical challenges and achieve commercial viability, leading to a cleaner energy future.



Solar Energy Technologies Office Progress and Goals Photovoltaics (PV) and Concentrating Solar-Thermal Power (CSP)

Figure 1.4 Comparison of achieved and targeted values for the levelized cost of electricity in solar energy technology by 2030 *[21]*.

1.3. Working principle of PSCs

The photoconversion efficiency of a solar cell depends on three key PV parameters: open circuit voltage (V_{oc}), short circuit current (J_{sc}), and fill factor (FF). Maximizing these parameters, which are interdependent and influenced by distinct physical properties, is essential for optimizing PV performance. However, the operational principles of PSCs are not as clearly understood as those of other solar cells.

The mechanism underlying the photovoltage generation in PSCs is complex and involves several key steps as shown in **Figure 1.5**.

- 1. Electron-hole pair generation by light absorption
- 2. Quasi-Fermi level splitting
- 3. Charge separation
- 4. Selective contacts
- 5. Built-in potential or kinetic exchange
- 6. Role of selective contacts



Figure 1.5 Energy band diagrams for a p-i-n solar cell at an open circuit subjected to (A) dark and (B) illuminated conditions, showing energy levels (E_{vac}, E_C, E_V, E_{F0}, E_{Fn}, E_{Fp}), electron charge, and built-in potential. (C) Energy losses and components in energy band diagram of DSSC *[22]*.

The mechanism of photovoltage generation in PSCs involves light absorption, electron-hole pair generation, quasi-Fermi level splitting, charge separation, selective contacts, and built-in potential or kinetic exchange. The initiation of energy conversion occurs when the perovskite material absorbs sunlight. This process elevates electrons from the valence band (VB) to the conduction band (CB), resulting in the generation of electron-hole pairs. These pairs are separated, minimizing recombination and contributing to the electrical current. Within the perovskite layer, quasi-Fermi levels are formed, indicating the energy states of electrons and holes when in a non-equilibrium condition. The disparity in the distribution of electrons and holes causes quasi-Fermi level splitting, which further differentiates their energy states. Charge separation generally takes place at the junction between the perovskite layer and the electron or hole transport layer (HTL), which is essential for optimizing the efficiency of solar cells [23]. Charge-selective contacts facilitate electron and hole extraction via built-in electric fields or kinetic exchange processes. Built-in potential mechanisms create an electric field due to differences in work functions between layers, aiding charge separation and photovoltage generation [24]. Kinetic exchange mechanisms involve selective contacts that transport one type of charge while blocking the other, enhancing charge extraction and preventing recombination [25]. The efficiency of charge extraction and overall device performance are significantly influenced by the choice of materials and interface engineering within the solar cell [26].

1.4 Photovoltaic parameters of PSC

The primary PV properties that define the operation of solar cells when exposed to light include V_{oc} , J_{sc} , power conversion efficiency (PCE), and FF. The J_{sc} is influenced by the mobility of charge carriers within the active layer and indicates the current density produced in the absence of an external bias. Jsc depends on the number of excitons generated and the incident light, with devices having wide absorption spectra achieving the highest J_{sc} due to more exciton collection from the solar spectrum [27]. The V_{oc} represents the highest voltage generated by a solar cell when no external current flows, and it is influenced by the Fermi energy levels of the working electrode and electrolyte. Due to charge carrier recombination, V_{oc} is generally lower than its theoretical maximum [28]. The FF quantifies the quality of a solar cell, defined as the ratio of the maximum power output to the product of V_{oc} and J_{sc} . It reflects the efficiency of charge extraction and generally varies between 0.6 and 0.85 due to transport losses and recombination [29]. The PCE is the ratio of the maximum power output to the power of the incident light, reflecting the device's efficiency in converting light energy into electrical energy [30]. The equations for FF and η are given as follows.



Figure 1.6 Schematic view of various photovoltaic parameters determined from a characteristic J-V curve of a solar cell.

$$\eta = \frac{P_{max}}{P_{in}} = \frac{FF \times Voc \times Jsc}{Pin}$$
 Eq. (2)

Where,

 V_m – Maximum value of voltage,

Isc - Short-circuit current,

 I_m – Maximum current value,

 η – Efficiency of the cell,

 V_t – Terminal voltage of the cell

 V_{oc} – Open-circuit voltage.

1.5. Literature survey

1.5.1. Perovskite solar cells

PSCs signify a groundbreaking advancement in the field of PVs, providing a compelling alternative to traditional silicon-based solar cells. Named after Russian mineralogist Lev Perovski, these cells are inspired by the mineral perovskite. The fundamental structure of a PSC consists of a thin-film absorber layer made of an organic-inorganic hybrid material featuring a perovskite crystal structure. This layer is sandwiched between electron and HTLs, facilitating efficient movement of charge carriers to their respective electrodes *[23]*. The core perovskite absorber layer absorbs sunlight, generating electron-hole pairs and initiating the PV process.

Several advantages are offered by PSCs over traditional siliconbased PV technologies. They exhibit higher power conversion efficiencies, with record efficiencies exceeding 25% [21]. Their solution-processable nature allows for low-cost, scalable fabrication methods, which can significantly reduce production costs and enable large-scale deployment. Additionally, PSCs perform well under lowlight conditions and wider angles of incident sunlight, expanding their applicability in various environmental settings. However, the environmental and health concerns surrounding lead, a common component in traditional perovskites, have driven the search for leadfree alternatives. Lead (Pb) exposure can lead to severe health issues, such as neurological disorders and organ damage, and lead pollution contributes to environmental degradation [31-33].

Pb-free perovskite materials present a sustainable pathway for renewable energy generation by eliminating toxic Pb compounds. By substituting Pb with elements such as tin or bismuth, these materials significantly reduce environmental contamination and health risks. Lead-free PSCs (LFPSC) also align with global efforts to transition towards cleaner energy sources, helping mitigate climate change and preserve natural resources. These materials offer comparable or even superior PV performance, with high power conversion efficiencies and long-term stability, and they can be manufactured using scalable and cost-effective processes. Additionally, the absence of Pb simplifies recycling and reduces the environmental impact of end-of-life solar panels [34-36].

1.5.2. Current State of Research

Challenges with Tin-Based Perovskites

Tin-based perovskites initially considered promising alternatives to Pb-based ones, face significant challenges in achieving high efficiency and stability due to the oxidation of Sn^{2+} to Sn^{4+} . This oxidation compromises the structural integrity and PV performance of the material, making long-term stability a significant challenge. Various approaches such as surface passivation, compositional engineering, and encapsulation techniques have been explored to address these issues, but the inherent instability of Sn^{2+} remains a critical hurdle [37,38].

Exploring Lead-Free Double Perovskites

Researchers have turned their attention to Pb-free double perovskite structures to overcome the limitations of tin-based perovskites. These materials involve substituting Pb²⁺ with M³⁺ cations like Bi³⁺, aiming to achieve Pb-free compositions while maintaining a three-dimensional perovskite structure. Despite the challenges posed by the higher charge of Bi³⁺ ions, recent advancements in the synthesis and characterization of double perovskites have shown promising results. Cs₂AgBiBr₆, for instance, has emerged as an intriguing candidate due to its favorable properties for various optoelectronic applications, including solar cells, radiation detectors, and sensors. However, challenges in film formation and device fabrication processes persist, limiting its scalability and commercial viability [39,40].

Recent Developments

A low-pressure assisted solution method was used by Wu et al. to produce stable, high-quality Cs₂AgBiBr₆ films. Their solar cell achieved 1.44% efficiency in a stable, Pb-free PSC. This provide the way for high-quality double perovskite layers, positioning Cs₂AgBiBr₆ as a contender for future solar cell technology [41]. Cs₂AgBiBr₆ thin films were produced by Wang et al. through sequential vapor deposition, resulting in a pure double perovskite phase with large grain sizes and a smooth surface. These films showed promise for solar applications with a PL lifetime of 117 ns. Solar cells achieved 1.37% efficiency and displayed stability under normal conditions. This method lays the groundwork for various optoelectronic devices [42]. Igbari et al. highlighted the superiority of solution-processed films over vacuum sublimation. This was attributed to precise composition stoichiometry achieved through solution processing. The solar cells achieved an impressive 2.51% efficiency [43]. Gao et al. used anti-solvent dropping technology which resulted in ultra-smooth Cs₂AgBiBr₆ films. High post-annealing temperatures were crucial for achieving excellent crystallinity. Solar cells achieved an impressive 2.23% efficiency, indicating potential in optoelectronic applications. The high thermal stability of the material suggests long-term device viability [44]. Wang et. al. demonstrated sensitization of the m-TiO₂ electron transport layer with enhanced Cs₂AgBiBr₆ PSCs. This led to increased optical absorbance, reduced defects, and enhanced electron extraction. The solar cells achieved a record 3.11% efficiency with a significantly increased short-circuit current density. Along with this, unencapsulated devices exhibited restrained hysteresis and excellent stability [45]. Furthermore, Yang et al. employed D149 indoline dye and Ti₃C₂T_x MXene to enhance the crystallization of Cs₂AgBiBr₆ where both contributed to the photocurrent. The weak van der Waals forces at the interface-maintained semiconductor properties and reduced Fermi level pinning. The carrier mobility was improved by the high work function of Ti₃C₂Tx, resulting in a PCE) of 4.47% under 1 sun and 7.23% under 2001x indoor light illumination, along with enhanced stability. This work highlights the potential of $Ti_3C_2T_x$ for double PSCs [46]. Wang et. al., combined Cs₂AgBiBr₆ with Zn-Chlorophyll (Zn-Chl) to serve as a sensitizing hole-transporting layer and achieved a record 2.79% PCE, 22–27% higher J_{sc} than devices using conventional HTLs. Zn-Chl played dual roles, acting as an HTL and photoactive layer, with a significantly higher extinction coefficient compared to other materials. This work marks a promising step towards eco-friendly solar cells [47]. Pb-free double perovskite Cs₂AgSbBr₆ with an indirect bandgap of 1.64 eV was synthesized by Wei *et al.* Single crystal X-ray diffraction (XRD) confirmed the Fm m space group and a lattice parameter 'a' of 11.1583(7) Å. The compound turned brown during post-heat treatment, maintaining symmetry and crystallinity. Further, the X-ray photoelectron spectroscopy (XPS) revealed Sb⁵⁺ presence, indicating charge transfer. UV-visible spectroscopy and DFT calculations probed optical and electronic properties [48].

Volatile salts were added by Wu et al. to control double perovskite crystallization, resulting in the formation of an organic/inorganic mixed intermediate phase, which was confirmed by XRD patterns. High-temperature annealing produced an all-inorganic double perovskite with a dense surface. The Cs2AgBiBr6 film demonstrated higher light absorption and emission, reduced trap density, and an extended carrier lifetime. The solar cell achieved 2.53% PCE, surpassing the control device. This work offers insights into Pb-free perovskite optoelectronics [49]. Fused-ring electron acceptor molecules were used by Li et al. to passivate defects in Cs₂AgBiBr₆ double PSCs, leading to an enhanced V_{oc} and PCE of 3.31%. The strong binding of FREA molecules reduced surface trap densities and non-radiative recombination. Furthermore, the passivated devices exhibited excellent long-term stability [50]. Zhang et al. utilized the hydrogenation method and adjusted the bandgap of Cs₂AgBiBr₆ films, improving the highest photoelectric conversion efficiency to 6.37%. This process also optimized carrier mobility and lifetime, offering a strategy for highperformance LFPSC [51]. Ghosh *et al.* synthesized organic-inorganic gold halide double perovskites with an ideal direct band gap, exhibiting good absorption coefficients and excellent charge transport properties. These perovskites displayed high chemical stability and photo response, showcasing the potential for optoelectronic applications [52]. Furthermore, Gruel *et al.* successfully fabricated Cs₂AgBiBr₆ films and integrated them into devices. The study emphasized the importance of high annealing temperatures for precursor conversion. PV devices incorporating Cs₂AgBiBr₆ films achieved high efficiencies and an exceptional V_{oc}, highlighting the potential of double perovskites [53]. Ning *et al.* demonstrated the first planar structure, Cs₂AgBiBr₆ double PSCs. The films exhibited high-quality grains and long electron–hole diffusion lengths, enabling the fabrication of efficient planar structure solar cells. This advancement represents a significant step towards environmentally friendly solar technology [54].

Table 1.1 Summa	ary of previous r	researcher	accomplishments	with their
methods used and	l solar cell paran	neters.		

Voc	Jsc	FF	PCE	Ref.
[V]	[mAcm ⁻		[%]	
	²]			
1.04	1.78	0.7	1.44	[41]
		8		
0.95	1.5	0.6	0.86	[42]
1.01	3.19	0.6	2.23	[43]
		9		
1.27	3.34	0.7		[44]
		75	3.31	
1.06	1.55	0.7	1.22	[45]
		4		
		•		
	Voc [V] 1.04 0.95 1.01 1.27 1.06	Voc Jsc [V] [mAcm ⁻ 2] 1.04 1.78 0.95 1.5 1.01 3.19 1.27 3.34 1.06 1.55	V_{oc} JscFF[V][mAcm ⁻ 2]2]1.041.780.780.951.50.61.013.190.69991.273.340.7751.061.550.741.550.7	V_{oc} Jsc FF PCE [V] [mAcm ⁻] [%] 2] - - 1.04 1.78 0.7 1.44 8 - - 0.95 1.5 0.6 0.86 1.01 3.19 0.6 2.23 9 - - - 1.27 3.34 0.7 - 1.06 1.55 0.7 1.22 4 - - -

One-step spin-coating with	1.02	1.84	0.6	1.26	[46]
Anti Solvent			7		
One-step spin-coating with	0.64	2.45	0.5	0.9	[47]
Anti Solvent			7		
One-step spin-coating with	0.71	1.67	0.5	0.68	[48]
Anti Solvent			7		
Sequential vapor deposition	1.12	1.79	NA	1.37	[49]
One-step spin coating	0.95	3.5	0.7	2.53	[50]
			6		
One-step spin coating with	0.92	11.4	0.6	6.37	[51]
antisolvent			0		
One-step spin coating	0.98	3.93	0.6	2.43	[52]
			3		
One-step spin coating	1.06	1.55	0.7	1.22	[53]
			4		
One-step spin coating	1.04	1.78	0.7	1.44	[54]
			8		

1.5.3. Current Challenges in LFPSC

Despite their potential, several challenges hinder the widespread adoption of LFPSCs:

1. Efficiency Limitations: LFPSCs still lag behind their Pb-based counterparts in terms of efficiency. The intrinsic properties of Pb-free materials, such as narrower band gaps and lower charge carrier mobilities, contribute to this limitation [55].

2. Stability Concerns: Long-term performance and environmental durability remain critical issues. Pb-free perovskite materials often exhibit inferior stability compared to Pb-based counterparts, leading to device degradation over time [56].

3. Material Toxicity: While Pb-free materials address the toxicity concerns of Pb, some alternatives may introduce new environmental and health hazards. Careful selection of replacement elements is necessary to balance optoelectronic properties with safety considerations [57].

1.5.4. Research Directions and Strategies

1. Material Design and Engineering: Optimizing the chemical composition and structure of Pb-free perovskite materials is essential to enhance their efficiency and stability. This includes exploring novel dopants, alloying strategies, and hybrid organic-inorganic architectures to improve electronic properties and mitigate degradation pathways.

2. Interface and Surface Engineering: Improving the interface between perovskite layers and charge transport materials can enhance device performance and stability. Surface passivation techniques, interfacial engineering, and defect management strategies are key to reducing recombination losses and improving charge extraction efficiency.

3. Stability Enhancement: Developing robust encapsulation methods and protective coatings can shield LFPSCs from environmental degradation factors such as oxygen, moisture, and light exposure. Understanding and mitigating ion migration phenomena can also enhance long-term stability and device reliability.

4. Scale-Up and Manufacturing: Streamlining fabrication processes and scaling up production methods are critical for the commercial viability of Pb-free PSCs. Developing scalable deposition techniques, optimizing ink formulations, and improving device reproducibility are essential for large-scale manufacturing.

Considering all the above factors here, the following objectives are proposed.

1.6 Objectives

- To investigate the impact of synthesis temperature of double perovskite Cs₂AgBiBr₆ on photoconversion efficiency.
- To synthesize the material at ambient conditions.
- To synthesize economical CuSCN as HTL to utilize in Cs₂AgBiBr₆ solar cell device.
- To characterize the ETL (TiO₂), AL (Cs₂AgBiBr₆), HTL (CuSCN) using the Physico-chemical measurements using XRD, FESEM, high-resolution TEM, XPS, etc.
- To study the Photoconversion efficiency of the device fabricated

Chapter 2

Experimental Techniques

2.1. Experimental Techniques

This chapter pertains to the methodologies employed in the fabrication of double perovskite $Cs_2AgBiBr_6$ and the characterization of materials proposed in this thesis.

2.1.1 Process of Spin coating

Spin coating is a commonly employed solution-based technique for depositing uniform thin films onto substrates using centrifugal force. This process involves spinning a solution of the material and solvent at high speeds, during which the surface tension and centripetal force of the liquid work together to produce a uniform layer ranging in thickness from a few nanometers to a few microns. This technique comprises four steps: spin up, deposition, spin-off, as well as evaporation, as illustrated in Figure 2.1 To begin, the Fluorine doped tin oxide (FTO) substrate is placed onto the vacuum turntable of the spin coater and a little amount of the solution material is coated onto the substrate. The solution is then distributed on the substrate by centrifugal force, and high spinning speeds cause the layer to thin. Following this, the layer is dried to remove volatile components and achieve uniform evaporation. In this research, a rotation speed of 3000 rpm for 30 seconds was utilized to obtain a uniform TiO₂ compact layer film with a thickness of approximately 80 nm [58]. The absorber layer and HTL were also deposited using this spin coating technique with the appropriate rotation speed.


Figure 2.1 Schematics of the spin-coating process and typical steps involved during the synthesis.

2.2. Design of double perovskite solar cells

The production of LFPSCs involves several steps. First, the FTO glass substrate is cleaned using ethanol, deionized (DI) water, and acetone to remove any contaminants. Then, a TiO₂ compact layer is synthesized and deposited onto the substrate. Next, the TiO₂ ETL layer was deposited onto the compact layer. After that, freshly synthesized Cs₂AgBiBr₆ in Dimethyl sulfoxide (DMSO) solution is spin-coated over the ETL layer. Which is then heated to get phase pure film with good quality. Finally, For the HTL layer Freshly prepared CuSCN solution in diethyl sulfide is spin coated over the Cs₂AgBiBr₆ layer. This multilayer device is subjected to DC sputter the Ag to complete the device.

Materials:

FTO is utilized as the substrate in the manufacturing process of solar cells, with titanium diisopropoxide bis(acetylacetonate) and titanium butoxide serving as precursors for the compact layer and TiO₂ ETL coating, respectively. Various solvents, including 1-butanol, DMSO, DI water, acetone, and ethanol, are employed. The synthesis of photo absorber layer $Cs_2AgBiBr_6$ involves the utilization of cesium bromide, bismuth tribromide, and silver bromide as precursors. All materials used in the process were sourced from Sigma-Aldrich and were of analytical grade, ensuring the highest market purity standards. They were employed without further refinement, playing a crucial role in ensuring the quality and reproducibility of the manufactured solar cells.

2.2.2. FTO glass substrate cleansing

The FTO-coated glass substrate was initially provided as a 100 mm x 100 mm sheet, then subsequently sectioned into smaller pieces measuring 15 mm x 15 mm. The cleaning process involved the following sequential steps:

1. FTO glass substrates were treated with ultrasonic waves in a bath of DI water for 15 minutes after being first cleaned with soap.

2. In the subsequent step, the substrates were subjected to ultrasonic treatment in acetone for a duration of 15 minutes to eliminate any residual grease, dust, and chemicals from the previous step.

3. Following that, the substrates underwent another ultrasonic treatment, this time in ethanol, for a duration of 15 minutes. This step was aimed at removing carbon-related impurities that may have accumulated on the surface during the acetone-cleaning process.

4. Finally, the substrates were dried using a hot air blower and then placed onto a hot plate set to 120 °C for 30 minutes. This step was intended to remove any residual organic solvents present on the substrates.

2.2.3. Fabrication of compact c-TiO₂ layer and TiO₂ ETL

The synthesis of TiO₂ began with the preparation of FTO substrates, which were cleaned in an ultrasonic bath containing soap, DI water, acetone, and ethanol to remove surface contaminants. The compact layer of TiO₂ (c-TiO₂) was synthesized by spin-coating a solution of Titanium diisopropoxide bis(acetylacetonate) in 1-butanol solvent at concentrations of 0.15M and 0.30M. The substrates were then heat-treated at 120°C for 30 minutes, followed by annealing at 450°C for 30 minutes to form a uniform and dense layer of c-TiO₂, serving as a seed layer for the TiO₂ ETL [59].



Figure 2.2 Schematic for the synthesis of TiO_2 layers on FTO coated glass substrate.

Two solutions were prepared: one comprising ethanol and Polyvinyl pyrrolidone (PVP) as a binder solution, and the other containing Titanium (IV) isopropoxide (TTIP), ethanol, and acetone as a precursor solution. Both solutions underwent stirring, mixing, and overnight aging before being filtered through a 40-micrometer syringe filter. The filtered solution was subsequently spin-coated onto the previously prepared compact layer. The coated substrates were then heated at 150°C for 30 minutes and annealed for 30 minutes in a muffle furnace at 450°C. The synthesis process is illustrated in **Figure 2.2**.

2.2.4. Preparation Cs₂AgBiBr₆ Powder



Figure 2.3. Synthesis procedure of Cs₂AgBiBr₆ powder.

In this synthesis, CsBr, BiBr₃, and AgBr were dissolved in 10 ml of HBr to create a homogeneous solution. The solution was then heated to 120°C on a hotplate with continuous stirring and maintained at this temperature for 3 hours to ensure complete reaction or dissolution. Upon completion, the reaction vial was removed from the hotplate and allowed to cool to room temperature, with further cooling in an ice bath to promote crystallization if necessary. The resultant crystalline solid was isolated washed with a small amount of ethanol, and then transferred to a clean, dry piece of filter paper to vacuum drier.

2.2.5. Preparation Cs₂AgBiBr₆ Film

In the synthesis process, previously synthesized Cs₂AgBiBr₆ crystal was dissolved in anhydrous DMSO, these chemicals were meticulously combined to form a 0.5 molar solution. Subsequently, the resultant mixture was vigorously stirred for one hour to ensure thorough dissolution. Following the dissolution phase, the solutions were heated to 70°C for a period of 10 minutes to ensure uniformity and promote chemical reactivity. Meanwhile, a substrate with a previously coated ETL layer is prepared for the subsequent coating process which is shown in **Figure 2.3** Solution-coating technique was used which is a two-step procedure. In the first step, the solutions were spin-coated onto the prepared substrates. This was followed by a second spin-coating step at 2500 rpm for 30 seconds to achieve the desired film quality and thickness.



Figure 2.4. Schematic illustration of the dissolution of Cs₂AgBiBr₆ powder in DMSO and spin-coating to prepare a Cs₂AgBiBr₆ layer.

2.2.6. Preparation of HTL

CuSCN weighed 35 mg and was dissolved in 1 ml of diethyl sulfide; after stirring for several hours, the resultant solution was then spin-coated over the CABB layer at 3000 rpm for 30 sec to get CuSCN film.

2.2.7. Contact

In this study, Ag was used as a contact and deposited using the DC sputtering method. The sputtering process lasted for 10 minutes, maintaining constant sputtering pressure, argon flow rate, and power at 1.0 W, 15 standard cubic centimeters per minute, and 5 millitorr, respectively. The working distance was approximately 10 cm. These optimized deposition conditions allowed for the deposition of Ag contact without causing significant damage to the HTL or compromising the interfacial quality between the HTL and Ag film. These components are susceptible to damage from particle impact or stress. Any deviation from the optimal deposition conditions would lead to increased series resistance and decreased parallel resistance.

2.3. Various Analytical and Characterization Techniques

2.3.1. Calculation of Fill Factor and Efficiency employing Current density – Voltage (J-V) curves

A Solar simulator instrument was utilized to measure the J-V characteristics of a 1cm x 1cm sample under a 1.5 G solar irradiation spectrum in both forward directions, using a 100 MW power as shown in **Figure 2.5**. To determine the stable PCE of solar cells, the power output was measured at a constant voltage near the maximum power point, while maintaining the device temperature at a constant 27°C. The primary aim of solar simulation technology is to create a laboratory-controlled indoor testing facility that closely resembles natural sunlight. A solar simulator is an apparatus that replicates sunlight in a laboratory setting, with a light source designed to have an intensity and spectral composition similar to that of sunlight.



Figure 2.5. Photo of the experimental setup of a solar simulator device.

2.3.2. X-ray diffraction (XRD)

For identifying crystalline materials, XRD is a popular and effective non-destructive technique. It gives detailed information on various structural parameters such as crystal structures, grain size, crystal defects, unit cell dimensions, and phases. X-rays are used in the XRD method to irradiate a sample, and the diffracted X-rays that interact with the crystalline structure of the sample are then measured. The atomic arrangement, crystal symmetry, and other structural details of the sample can be obtained by analyzing the diffracted X-ray pattern.

Working Principle:

The crystal structure of a material functions as a threedimensional diffraction grating for X-ray wavelengths. When X-rays are directed at a sample, they are scattered from an array of the lattice planes within the crystal structure at particular angles. If the scattered beams interfere constructively, XRD peaks are formed. The distribution of atoms within the lattice determines the intensity of the peaks, which is unique to the crystal structure. Thus, XRD serves as a fingerprint of periodic atomic arrangements. Bragg's law describes the condition for constructive interference, relating the X-ray angle of incidence to the spacing between lattice planes and the order of diffraction. The equation for Bragg's law can be used to determine the crystal structure of a material by analyzing the positions and intensities of the XRD peaks.

$$n\lambda = 2 d_{hkl} \sin \theta$$

where 'n' represents the order of diffraction (an integer greater than zero), ' λ ' signifies the wavelength of the incident X-ray, 'd' signifies the interplanar distances of the lattice planes indexed by (h,k,l) & ' θ ' represents the angle of incidence of the X-ray beam with respect to the lattice planes. **Figure 2.6** depicts the XRD obtained from the crystal lattice.



Figure 2.6 Schematic for the working principle of XRD and demonstration of Bragg's law [60].

Instrumention:

An X-ray diffractometer consists of three primary components: an X-ray tube, a sample holder, and a detector. The cathode ray tube filament is heated to produce electrons, which are then accelerated towards a target material by applying a voltage. The collision of electrons with the target material dislodges inner shell electrons, generating characteristic X-ray spectra. Copper is commonly used for single-crystal diffraction because its K α radiation has a wavelength of λ = 1.5418 Å. The collimated X-ray beam is directed at the sample, which is rotated along with the detector to measure the intensities of reflected X-rays. Constructive interference of reflected rays results in a peak in intensity. The detector captures the X-ray signal, converts it to a count rate, and provides the output to the user. The collimated X-ray beam strikes the rotating sample at an angle θ , and the detector collects the diffracted beams while rotating at an angle of 2 θ .



Figure 2.7 X-ray diffractometer setup and its basic components [61].

2.3.3. Field Emission Scanning Electron Microscope (FESEM)

The FESEM is an imaging method that employs a focused electron beam to get high-resolution images of solid samples. In addition to imaging, FESEM can also be used for elemental analysis of the sample. The most commonly used imaging mode in FESEM is the secondary electron image, which provides a map of secondary electron emissions as a function of spatial position. The topography of the sample may be visualized by using this emission intensity, which depends on the angle among the surface and the beam. **Figure 2.8** shows an example of a secondary electron image obtained using SEM.

Working Principle

When primary electrons are directed toward the sample in SEM, they generate low-energy secondary electrons. The detection and mapping of these secondary electrons offer insights into the topography of the specimen.

Instrumentation

The electron optical system serves as the primary method for generating a probe electron beam, comprising an electron gun, condenser lens, objective lens, and scanning coil. The electron gun produces the electron beam, while the lenses focus and adjust the beam's diameter. Additionally, a specimen stage is incorporated into the system for holding the specimen being analyzed, and a secondary electron detector is employed for collecting secondary electrons emitted from the specimen. The resulting data is then transformed into an image format and displayed on a display unit that is connected to an operating system, which allows for various operations to be carried out.



Figure 2.8 Schematic illustration of the working principle of the FESEM and its basic construction including typical components *[62]*.

2.3.4 X-ray photoelectron spectroscopy (XPS)

The XPS, also called electron spectroscopy for chemical analysis (ESCA), is an analytical method used to investigate the chemical composition and electronic state of solid surfaces. In XPS, a sample is irradiated with X-rays, which eject photoelectrons from the surface. The kinetic energy and corresponding binding energy of these emitted electrons are then analyzed, offering insights into the elemental composition, chemical bonding, and oxidation states of the atoms in the sample.

Working Principle

When X-rays bombard the surface of a material in XPS, they excite core-level electrons, causing them to transition to higher energy states or even to be ejected from the atom entirely. The energy of the emitted photoelectrons is distinctive to the specific element and its chemical environment. By measuring the kinetic energy of these electrons, the binding energy can be determined, allowing the inference



of the chemical composition and electronic structure of the sampl

Figure 2.9 Basic experimental setup and working principle of XPS and involved components *[63]*.

Instrumentation

The components of an XPS instrument are an X-ray source, an electron energy analyzer, and a detector. Typically X-ray source employs a monochromatic X-ray beam generated from an X-ray tube or a synchrotron radiation source. This X-ray beam is directed onto the sample surface, inducing the photoemission of electrons. The emitted electrons are then collected by an electron energy analyzer, such as a hemispherical analyzer, which separates them based on their kinetic energy. Finally, the intensity of the emitted electrons is recorded by a detector based on their kinetic energy. This process generates a spectrum

that displays the elemental composition and chemical states on the sample surface as illustrated in **Figure 2.9**

In addition to these core components, an XPS instrument may also include various accessories and peripherals, such as a sample stage for positioning and manipulating the sample, a charge neutralizer to mitigate charging effects on insulating samples, and a computer system for data acquisition, analysis, and visualization.

2.3.5 Raman spectroscopy

Raman spectroscopy is an analytical method that involves the interaction of light with matter to offer comprehensive data about a sample's molecular structure and composition. In addition to elucidating molecular properties, Raman spectroscopy can also be employed for chemical identification and analysis. The most common mode of operation in Raman spectroscopy is the collection of Raman scattered light, which is generated when incident light interacts with molecular vibrations within the sample. This scattered light carries information about the vibrational modes of the molecules, enabling the characterization of chemical bonds and functional groups present in the sample.

Working Principle

When a monochromatic light source, such as a laser, illuminates a sample, inelastic scattering of some incident photons occurs due to interactions with molecular vibrations. This results in a frequency shift in the scattered photons, termed the Raman shift, which reflects the energy associated with the sample's vibrational modes. By examining the intensity and frequency of these scattered photons, one can obtain



valuable insights into the sample's chemical composition and structure.

Figure 2.10 Schematic demonstration of RAMAN spectroscopy technique and its working mechanism *[64]*.

Instrumentation

Raman spectroscopy typically involves a laser as the excitation source, which provides a monochromatic and coherent light beam. The scattered light is then collected and analyzed using a spectrometer equipped with a diffraction grating or a dispersive element to separate the different wavelengths. Additionally, the intensity of the scattered light at each wavelength is measured using a detector. The data obtained is then processed and transformed into a Raman spectrum, displaying the intensity of Raman scattered light as a function of the Raman shift. This spectrum can then be interpreted to extract valuable information about the molecular composition and structure of the sample under investigation as illustrated in **Figure 2.10**.

2.3.6 UV-Visible spectroscopy

Transitions between electronic energy levels are primarily responsible for the visible /ultraviolet (210–900 nm) electromagnetic radiation absorption. Light in this spectral region is absorbed as a result of such transitions. The most common electronic transition in this range

is from the highest occupied molecular orbital (HOMO) or VB to the lowest occupied molecular orbital (LUMO) or CB.

This method is especially helpful in determining the band-gap of semiconducting materials. A UV-Vis spectrometer is commonly employed for this purpose, and its experimental set-up typically involves a sample compartment where the sample is placed, a light source that emits light in the UV-Vis range, a monochromator for selecting a specific wavelength of light, a cuvette to hold the sample, and a detector to measure the intensity of the transmitted light. The band-gap of the semiconducting material can be calculated utilizing the data from this Figure 2.11 depicts UV-Vis experiment. the spectrometer experimentation setup.



Figure 2.11 Typical schematic experimental setup of UV-Visible spectroscopy, its working mechanism, and various components [65].

2.3.7 Atomic force microscopy (AFM)

The surface topography, mechanical properties, and interactions at the atomic or molecular level are investigated by researchers using AFM, a high-resolution imaging technique. Unlike traditional microscopy methods that rely on optical or electron beams, AFM uses a mechanical probe to scan the surface of a sample, generating detailed three-dimensional images with nanometer-scale resolution.

Working Principle

By scanning a sharp tip, typically made of silicon or silicon nitride, over the surface of a sample, AFM operates. The tip is attached to a flexible cantilever that bends in response to the forces between the tip and the sample surface. These forces can include van der Waals forces, electrostatic forces, and other short-range interactions.

Instrumentation

An AFM system comprises several key components:

1. Cantilever and Tip: The cantilever, a flexible beam with a sharp tip at its end, is essential for high-resolution imaging. The sharpness of the tip is crucial for achieving detailed images. Silicon and silicon nitride are commonly used materials for the tip and cantilever due to their stiffness and durability.

2. Laser and Photodetector: On the back of the cantilever a laser beam is focused, and its reflection is detected by a photodetector. Changes in the cantilever's position cause variations in the laser reflection, which are used to measure surface topography.

3. Piezoelectric Scanner: This component moves the sample or the cantilever in very precise increments in the x, y, and z directions. The scanner is typically made of piezoelectric materials that expand or contract in response to an applied voltage, allowing for sub-nanometer precision.

4. Feedback Control System: The interaction force between the tip and the sample is kept constant by the feedback loop, which adjusts the height of the cantilever accordingly. This system ensures accurate topographical measurements by compensating for variations in sample height.

5. Computer System: The AFM is controlled by a computer system that manages data acquisition, image processing, and visualization. Advanced software algorithms are used to convert the raw data from the photodetector into detailed images and quantitative measurements of surface properties.

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Figure 2.12 Schematic illustration of the basic construction including typical components of AFM *[66]*.

Working Mechanism

When the AFM tip approaches the sample surface, it encounters different forces that vary based on closeness. At close distances, repulsive forces prevail due to the Pauli exclusion principle and electrostatic interactions. As the distance increases slightly, attractive van der Waals forces become significant. These forces cause the cantilever to bend or deflect. A laser beam, reflected off the cantilever's back and directed onto a position-sensitive photodetector, measures this deflection. The photodetector then records changes in the laser beam's position, corresponding to the cantilever's deflection. To ensure a constant force between the tip and the sample, a feedback loop is utilized. This system adjusts the cantilever's vertical position using a piezoelectric scanner, maintaining consistent interaction force while the tip scans the surface. Such adjustments allow the tip to accurately follow the surface contours. The piezoelectric scanner enables precise movements of the sample or cantilever in the x, y, and z directions, facilitating sub-nanometer resolution. During the scanning process, deflection data from the cantilever is collected and used to create a highresolution topographical map of the surface. The data from the

photodetector is processed by a computer system, which converts the cantilever deflections into a three-dimensional image of the sample surface. Advanced software algorithms enhance the image quality and allow for quantitative analysis of surface properties.

As illustrated in **Figure 2.12**, the AFM's ability to provide highresolution, three-dimensional images and its capability to measure various surface properties make it an indispensable instrument in modern scientific research.

2.3.8 Transmission Electron Microscopy (TEM)

TEM is a highly effective technique for visualizing the internal structures of materials on an atomic or molecular scale. By transmitting an electron beam through an ultra-thin specimen, TEM generates images with high resolution, offering detailed insights into the sample's morphology, crystallography, and elemental composition.

Working Principle

TEM operates by directing a high-energy electron beam through an extremely thin specimen. The sample interacts with the electrons, causing them to be scattered or transmitted. This process forms an image that reveals the material's internal structure. The high energy of the electrons (typically 100-300 keV) allows them to penetrate the sample and produce detailed images with resolutions down to the atomic level.

TEM Instrumentation

A TEM system comprises several key components:

1. Electron Gun: The source of the electron beam is the electron gun. It may use a tungsten filament, LaB_6 crystal, or field emission source, each providing different levels of brightness and coherence.

2. Electromagnetic Lenses: These lenses focus and control the electron beam. The condenser lenses adjust the beam's size and convergence, while the objective lens forms the initial image. Intermediate and projector lenses further magnify the image. 3. Sample Holder: The sample holder positions the thin sample in the pathway of the electron beam. It allows for precise control of the sample's orientation and positioning.

4. Vacuum System: TEM operates under high vacuum conditions to prevent electron scattering by air molecules and to protect the electron gun and lenses. The vacuum system includes pumps and valves to maintain the required vacuum levels.

5. Imaging System: The transmitted electrons form an image that can be visualized on a fluorescent screen, recorded on photographic film, or captured by a digital camera. Modern TEMs use high-resolution cameras for digital imaging and analysis.

6. Computer System: The TEM is controlled by a computer system that manages data acquisition, image processing, and analysis. Advanced software algorithms enhance image quality, perform quantitative analysis, and facilitate data interpretation.



Figure 2.13 Simplified TEM diagram showcasing the key components *[67]*.

As illustrated in **Figure 2.13**, TEM's ability to provide highresolution, detailed images of internal structures at atomic or molecular scales makes it a critical instrument in modern scientific research.

Working Mechanism

The electron beam is produced by an electron gun, which commonly uses a tungsten filament, LaB₆ crystal, or a field emission source. The gun emits electrons when heated or subjected to a strong electric field. The emitted electrons are accelerated to high energies by an electric field, creating a coherent beam of electrons. The acceleration voltage typically ranges from 100 to 300 kilovolts (kV). The electron beam, once accelerated, is concentrated and aimed at the sample with the help of several electromagnetic lenses and apertures. These lenses manage the beam's coherence and convergence, guaranteeing that a precise, well-focused beam interacts with the sample. The electron beam passes through the thin sample. As electrons traverse the sample, they interact with the atoms, undergoing scattering and diffraction. These interactions depend on the atomic structure and composition of the sample. After passing through the sample, the transmitted and scattered electrons are focused by additional electromagnetic lenses to form an image. The image is magnified and projected onto a fluorescent screen, photographic film, or a digital camera, allowing for visualization and analysis. The resulting image provides detailed information about the sample's internal structure. Advanced software algorithms are used to enhance image quality and extract quantitative data on sample morphology, crystallography, and composition.

Chapter 3

Results and Discussion

This chapter deals with the results of the Cs₂AgBiBr₆ materials characterization and its performance testing. The results obtained from diverse physicochemical characterizations, such as FESEM, XRD, Raman spectroscopy, and UV-Visible spectroscopy, are compiled in this chapter. Initially, morphological and structural properties of TiO₂, prepared through the spin coating method, are discussed, followed by investigations into the photo absorber properties. Lastly, the performance of the fabricated Pb-free double PSC, comprising FTO/c-TiO₂/m-TiO₂/Cs₂AgBiBr₆/CuSCN/Ag, is examined.

3.1. Investigation of TiO₂ layer

TiO₂ is commonly used as the ETL PSCs due to its high thermal stability, low cost, and suitable energy level. The TiO₂ layer plays a crucial role in the PSCs, it plays a dual role in the device. Firstly, it acts as a compact layer just on the top of the FTO substrate and helps to avoid the leakage of current/electrons directly to the substrate. The carrier recombination at the interface between the FTO and perovskite layers is prevented by a TiO₂ compact layer, also referred to as a blocking layer, which plays a vital role in PSCs. Secondly, the mesoporous/rod like morphology with a high specific area grown will help to separate the electron from the absorber layer ($Cs_2AgBiBr_6$). Controlling its purity and thickness both are important as they affect the solar cell performance.

3.1.1. XRD analyses of TiO₂ layer



Figure 3.1. XRD pattern of spin-coated TiO₂ ETL on FTO substrates.

The XRD pattern of the TiO₂ layer spin-coated onto the FTO substrate is depicted in **Figure 3.1**. All diffraction peaks match the JCPDS card No. 21–1276, confirming the tetragonal rutile phase formation of TiO₂. No impurity peaks appeared in the XRD pattern confirming the phase purity of the synthesized TiO₂ material. The calculated lattice parameters are $a = 3.771 \pm 0.005$ Å and $c = 9.572 \pm 0.003$ Å, which are in good agreement with existing literature.

3.1.2. FESEM Analyses of TiO₂

Figure 3.2 shows the FESEM images of the TiO_2 ETL coated on a glass substrate. **Figure 3.2(a)** displays the surface morphology of the FTO substrate, which is very dense and compact indicating good surface coverage. **Figure 3.2(b)** represents a compact TiO_2 layer deposition with good coverage. **Figure 3.2(c)** shows the FESEM image of the TiO_2 ETL layer, revealing a uniform deposition of mesoporous- TiO_2 layer over the compact layer which is crucial for optimal device performance. Moreover, EDS analysis confirms that the composition of the TiO_2 layer aligns with its expected stoichiometry of Ti and O. The respective elemental composition and color mapping are shown in **Figure 3.2(d)**, which also shows the uniformity of the film.

Glacial acetic acid is employed as a stabilizing agent to prevent hydrolysis during the synthesis of TiO₂. The strong affinity of Ti⁴⁺ with water necessitates prior stabilization to prevent hydrolysis. Therefore, glacial acetic acid is utilized as a stabilizing agent and catalyst during TiO₂ synthesis. Through condensation, Ti(OBu)₄ is stabilized by acetic acid, leading to the formation of continuous chains with a high surface area. The combination of glacial acetic acid and PVP, employed as a binder in synthesis, facilitates the uniform growth of a TiO₂ layer on a glass substrate. The presence of Ti and O without any foreign species is verified through EDS and elemental mapping spectra, which exhibit uniform distribution across the surface, ensuring highly stable structural, morphological, and chemical properties of the grown TiO₂ layer.



Figure 3.2. Surface morphology and compositional analysis were performed with FESEM and top view images of (a) bare FTO, (b) compact TiO_2 layer, (c) TiO_2 ETL layer (d) EDS spectra of TiO_2 layer

(inset: color mapping of TiO_2 film showing uniform distribution of Ti and O across the sample).

3.1.3. UV-Vis spectroscopy analysis of TiO₂

UV-visible absorption spectroscopy was performed to examine the optical band-gap of TiO₂ ETL. The absorption spectra of TiO₂ were recorded in between 200 to 800 nm, and the bandgap energy was determined using the Tauc plot. A distinct absorption peak was observed at around ~378 nm, enabling the calculation of the band gap of rutile TiO₂. These results are illustrated in **Figure 3.3(a)**, with the corresponding Tauc's plot displayed in **Figure 3.3(b)**.



Figure 3.3 (a) Absorption spectra of TiO₂ electron transfer layer and (b) Bandgap estimations from Tauc plot corresponding to TiO₂ ETL.

The bandgap of the synthesized TiO₂ ETL was found to be 3.48 eV, as demonstrated in **Figure 4(b)**, aligning closely with the theoretical value of 3.2 eV. This deviation may be due to different morphological aspects. It is therefore suggested that the UV light absorption and transmission across the entire visible spectrum are effectively facilitated by the synthesized TiO₂ ETL [68,69].

3.1.4 Raman spectroscopic analysis of TiO₂

Raman spectroscopy was utilized to ascertain the formation of TiO_2 and to assess the phase composition of the resulting material. In the lattice structure of rutile, two TiO_2 units are present, with Ti^{4+} ions positioned at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), and O^{2-} ions occupying positions

at \pm (u, u, 0) and \pm (½+u, ½-u, ½). The rutile crystal structure exhibits Raman active modes namely B_{1g}, multi-phonon process, A_{1g}, and E_g. The distinctive Raman active modes of rutile phase TiO₂, namely B_{1g}, A_{1g}, and E_g, were detected at frequencies of 144.6, 448.3, and 609.4 cm⁻¹, respectively, as illustrated in **Figure 3.4**.

Additionally, a supplementary peak at 244.3 cm⁻¹ was observed, ascribed to a multi-photon phenomenon. The symmetric O-Ti-O bending and stretching vibrations are represented by the B_{1g} and E_g peaks, respectively, while the A_{1g} peak signifies another predominant vibrational mode. The prominent and broad peak at 240.9 cm⁻¹ is due to the multiphoton process, stemming from photon scattering, in alignment with prior literature.



Figure 3.4. Raman spectra of the TiO_2 ETL layer prepared on FTO substrate.

3.1.4. Atomic force microscopy (AFM) of TiO₂

The AFM topography image of TiO_2 is shown in **Figure 3.5(a)**, which reveals a smooth surface morphology with nanoscale grains and

height variations up to 43.2 nm, indicating low surface roughness, which further helped to get a smooth absorber layer. **Figure 3.5(b)** presents the line profile analysis of the AFM image, which shows minor height fluctuations along a line chosen for profiling, corresponding to the surface grains. **3.5 (c)** provides a 3D AFM image, offering a detailed perspective on the surface topography.



Figure 3.5 AFM analysis of TiO₂ film (**a**) topography image, (**b**) line profile analysis, (**c**) 3D AFM image, and (**d**) Ra and Rq roughness analysis.

The 3D visualization confirms the presence of relatively smooth grains and shallow valleys, with heights reaching up to 43.2 nm. The roughness analysis **3.5** (d) shows an average roughness (Ra) of approximately 2.56 nm and a root mean square roughness (Rq) of approximately 3.23 nm.

The low roughness of the film facilitated efficient charge transport through the ETL layer. Additionally, the uniform deposition of the absorber layer, resulting in minimal surface roughness, is achieved through the contribution of the TiO_2 compact layer to film quality enhancement.

3.2. Investigation of Cs₂AgBiBr₆ powder



3.2.1. XRD of Cs₂AgBiBr₆ powder

Figure 3.6 Rietveld refined XRD pattern of the Cs₂AgBiBr₆ powder.

The Rietveld refined XRD pattern of the Cs₂AgBiBr₆ powder is displayed in **Figure 3.6.** XRD peaks match with JCPDS File number 01-084-8699, confirming the growth of phase pure Cs₂AgBiBr₆. All observed peaks are in good agreement with the cubic phase of Cs₂AgBiBr₆, indicating successful pure-phase formation. The detailed analysis of the XRD data revealed the estimated lattice constant of (a =11.210 ± 0.003) Å, which is in agreement with values reported in earlier studies.

3.2.2. FESEM images of Cs₂AgBiBr₆ powder

Figure 3.7(a) shows the FESEM image of $Cs_2AgBiBr_6$, indicating the well grown grains with distinct sizes. Figure 3.7(b) shows $Cs_2AgBiBr_6$ crystal in octahedral shape with different sizes distribution with majority of them lying in a range of 1-2 μ m. Figure 3.7(c) represents EDS mapping with the atomic weight distribution of 59.1, 21.2, 10.3, and 9.4 % of Br, Cs, Ag, and Bi, respectively, indicating the stoichiometric integrity of crystals.





3.2.3. UV-Vis spectroscopy analyses of Cs2AgBiBr6 powder

To obtain the absorption range and estimate the band gap of the $Cs_2AgBiBr_6$ material, UV-Visible spectroscopy was performed. As depicted in **Figure 3.8(a)**, the absorption spectra of $Cs_2AgBiBr_6$ were scanned in the range of 400 to 800 nm, showing effective visible light absorption in the 400 to 600 nm range. The absorption spectra are very important in order to understand the performance of the PSC. Further, estimating the bandgap of the $Cs_2AgBiBr_6$ is also essential for understanding how much energy is required for producing electron-hole pairs and the charge transfer mechanism. To do so, we plotted Tauc's plot and calculated the band gap of the $Cs_2AgBiBr_6$ film via $(\alpha h \upsilon)^{1/2}$ —h υ relation which is 2.17eV and shown in **Figure 3.8(b**).



Figure 3.8. (a) UV-visible spectrum of Cs₂AgBiBr₆, and (b) Tauc plot for estimating the bandgap of Cs₂AgBiBr₆.

3.2.4. Raman spectroscopy analysis of Cs₂AgBiBr₆ powder

Figure 3.9 shows the Raman spectra of Cs₂AgBiBr₆. The experimental results closely align with previously reported data, facilitating precise peak assignment through symmetry analysis. Specifically, within the Cs₂AgBiBr₆ compound, three distinct Ramanactive modes have been identified: F_{2g} , E_g , and A_{1g} , as illustrated in the provided Raman spectrum. The F_{2g} mode at 76.5 cm⁻¹ is associated with the scissoring motion of bromine relative to cesium, reflecting the bending vibrations in the lattice structure. This motion involves the movement of Br atoms in a plane perpendicular to the bond axis, indicative of the flexible nature of the Cs-Br bond and the dynamic structural environment within the perovskite lattice. The Eg mode at 136.4 cm⁻¹ indicates the asymmetric stretching of [AgBr6]⁻⁵ octahedra, where bromine atoms move in opposite directions along different axes. This mode highlights the presence of uneven bond lengths and angles within the octahedra, suggesting a degree of structural distortion that impacts the electronic properties of the material. The prominent A_{1g} mode at 181 cm⁻¹ is linked to the symmetric stretching of [AgBr6]⁻⁵ octahedra, involving in-phase movements of bromine atoms along the bond axis, resulting in significant changes in polarizability and strong Raman activity. This symmetric stretching mode is crucial as it reflects the uniform expansion and contraction of the Ag-Br bonds, directly influencing the material's vibrational coherence and stability. These

observations confirm the crystalline quality and symmetry of $Cs_2AgBiBr_6$ films, enhancing comprehension of their structural dynamics and vibrational characteristics.



Figure 3.9 Raman spectra of Cs₂AgBiBr₆.

3.2.5. XPS analysis of Cs2AgBiBr6 powder



Figure 3.10 (a) Survey scan of $Cs_2AgBiBr_6$, high-resolution scans of (b) C1s, (c) Cs 3d, (d) Ag 3d, (e) Bi 4f, and (f) Br 3d.

To determine the elemental composition and chemical state of this material, an XPS analysis was conducted. The XPS survey spectra, shown in **Figure 3.10(a)**, reveal the presence of Cs, Ag, Bi, and Br elements in the examined double perovskite sample. **Figure 3.10(b)**

presents the C1*s* peak at 284.8 eV, indicating no spectral shift. Additionally, high-resolution spectra for Cs 3*d*, Ag 3*d*, Bi 4*f*, and Br 3*d* core levels display distinct peaks. The peaks at binding energies of 723.4 eV and 737.5 eV are attributed to Cs $3d_{5/2}$ and $3d_{3/2}$ core levels, respectively **Figure 3.10(c)**. Similarly, peaks at 367.3 eV and 373.4 eV correspond to Ag $3d_{5/2}$ and $3d_{3/2}$ core levels, respectively **Figure 3.10(d)**. The binding energies of 160.7 eV and 166.2 eV are ascribed to Bi $4f_{7/2}$ and $4f_{5/2}$ core levels, respectively **Figure 3.10(e)**. Finally, peaks at 67.6 eV and 69.6 eV are associated with Br $3d_{5/2}$ and $3d_{3/2}$ core levels, respectively **Figure 3.10(f)**. These results are in agreement with previous reports on Cs₂AgBiBr₆ thin films and confirm the sample's purity.





Figure 3.11 (a)TEM image of Cs₂AgBiBr₆. (b) high-resolution TEM image of Cs₂AgBiBr₆.

TEM study was employed to analyze the formation of $Cs_2AgBiBr_6$ crystals. Figure 3.11(a) shows a TEM image, while Figure 3.11(b) presents a high-resolution TEM image of the $Cs_2AgBiBr_6$. The high-resolution TEM image reveals interplanar spacings of 0.309 nm and 0.416 nm, corresponding to the (004) and (022) lattice planes, respectively. These observations are consistent with the XRD pattern shown in Figure 3.6.

3.3. Investigation of Cs₂AgBiBr₆ layer

The results of evaluating $Cs_2AgBiBr_6$ synthesized on TiO_2 ETL under various reaction conditions are delineated in this section. Characterization was conducted utilizing a range of methods including FESEM, XRD, Raman spectroscopy, and UV-Vis spectroscopy.

3.3.1. XRD analysis of Cs₂AgBiBr₆ film

After the spin coating of the Cs₂AgBiBr₆ layer, we heated it at five different temperatures (i.e., 200, 225, 250, 275, and 300°C) to understand its formation and phase purity behavior. To determine the lattice parameters and phase purity, the XRD patterns of all Cs₂AgBiBr₆ samples treated at different temperatures were performed and shown in **Figure 3.12**. As visible in the XRD patterns of the Cs₂AgBiBr₆ samples treated at 200, 225, and 250°C, there is one extra peak arising at 30.9° and attributed to the Cs₃Bi₂Br₉, i.e., mixed phase formation takes place. This reflects that the optimum temperature of heating to obtain phase pure Cs₂AgBiBr₆ must be more than 250°C. Therefore, the prepared Cs₂AgBiBr₆ layer which can be used for further processing. The film heated at 300°C shows the unidentified impurity peak and deviates from phase purity.



Figure 3.12 XRD pattern of the Cs₂AgBiBr₆ films heat treated at 200°C, 225°C, 250 °C, 275 °C, and 300°C.

The diffraction peaks observed were indexed as (111), (002), (022), (222), (113), (004), (113), (024), (224), (044), (244), (026), and (444), indicating the cubic crystalline structure of $Cs_2AgBiBr_6$. The cell unit parameter was determined to be 10.201 ± 0.002 Å, which is consistent with $Cs_2AgBiBr_6$ powder.

3.3.2. FESEM Analysis of Cs2AgBiBr6 Films

To check the effect of temperature on the Cs₂AgBiBr₆ morphology, we have performed FESEM of all the samples, and their results are depicted in **Figure 3.13**. As visible from the below figure, as the heating temperature increases from 200°C to 275°C, Cs₂AgBiBr₆ morphology gets smoother and shows uniform coverage throughout the surface **Figure 3.13.(d)**. However, above 275°C, the surface coverage again gets worse. Further, the best morphology sample was analyzed for their composition, and EDS spectra were performed. The EDS spectra of Cs₂AgBiBr₆ film heated at 275°C is shown in **Figure 3.13.(f)**. The obtained atomic percentages of Cs, Ag, Bi, and Br elements are 64.9, 15.7, 10.6, and 8.8%. In all the samples, only the Cs₂AgBiBr₆ sample

heated at 275°C is totally pinhole free, and shows smoother, dense grains with uniform surface coverage which is essential for stable and efficient LFPSC.



Fig 3.13 FESEM images of the Cs₂AgBiBr₆ film coated on TiO₂ substrate and heated at (a) 200 °C, (b) 225°C, (c) 250 °C, (d) 275 °C, (e) 300 °C, and (f) EDS spectra of Cs₂AgBiBr₆ film heated at 275°C.

3.3.3. UV analysis of Cs2AgBiBr6 film



Figure 3.14 (a) UV-visible spectroscopy of the Cs₂AgBiBr₆ film at 225, 250, and 275 °C and **(b)** Tauc plot for estimating the bandgap of the material.

As depicted in **Figure 3.14(a)**, the absorption spectra of the $Cs_2AgBiBr_6$ film were scanned in the range of 400 to 800 nm, revealing effective visible light absorption in the 400 to 600 nm range. The absorption spectra for $Cs_2AgBiBr_6$ films treated at different

temperatures (225°C, 250°C, and 275°C) show notable variations. The absorption edge shifts towards longer wavelengths (redshift) as the temperature increases, indicating a change in the band gap energy. Specifically, the films exhibit characteristic absorption peaks, whose intensity and position vary with the treatment temperature. These changes result from the variations in the film's crystallinity and grain size due to thermal treatment. Increasing the temperature can increase the film's crystallinity and expand the grain size, which reduces defect states and enhances optical properties. This results in a more pronounced absorption edge and potentially higher absorbance in the visible range. The redshift in the absorption edge with increasing temperature suggests a decrease in the band gap energy, which is indicative of changes in the film's electronic structure.

The Tauc plot, which involves plotting $(\alpha hv)^{1/2}$ versus hv, was utilized for the estimation of band gap of Cs₂AgBiBr₆ films. **Figure 3.14(b)** shows the Tauc plots for films treated at different temperatures, with the band gap values estimated to be approximately 2.36 eV for the film treated at 225°C, 2.2.37 eV for the film treated at 250°C, and 2.2.38 eV for the film treated at 275°C. These values indicate that the band gap slightly increases with temperature. As temperature increases, the lattice parameters, defect densities, and electronic structure of the films are altered. This can lead to slight increases in the band gap, as observed in the Cs₂AgBiBr₆ films.

3.3.4. XPS of Cs₂AgBiBr₆ films coated on TiO₂



Figure 3.15 (a) Survey scan, high resolution XPS data of (b) C 1*s*, (c) Ca 3*d*, (d) Ag 3*d*, (e) Bi 4*f*, (f) Br 3*d*, (g) Ti 2*p*, (h) O 1*s* of Cs₂AgBiBr₆ films coated on TiO₂.

The XPS analysis of Cs₂AgBiBr₆ coated on a TiO₂ film offers comprehensive insights into the material's elemental composition and chemical states. The XPS survey spectrum in Figure 3.15(a) confirms the presence of Cs, Ag, Bi, and Br in the double perovskite CABB layer on TiO₂ film with Ti and O. The carbon C 1s peak at 284.8 eV in Figure **3.15(b)** serves as a reference point, indicating no significant spectral shift and confirming calibration accuracy. Additionally, a peak at 288.43 eV is attributed to the O-C=O group, indicating adsorbed carbon on the surface of the film. High-resolution XPS spectra offer precise insights into the core levels of the individual elements. The Cs 3d core levels in Figure 3.15(c) show Cs $3d_{5/2}$ and Cs $3d_{3/2}$ peaks at binding energies of 723.4 eV and 737.3 eV, respectively, consistent with Cs in the Cs₂AgBiBr₆ layer. The Ag 3*d* core levels exhibit Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks at 367.35 eV and 373.4 eV as shown in Figure 3.15(d), indicating Ag in a stable oxidation state of +2. The Bi 4f core levels in Figure 3.15 (e) present Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks at binding energies of 158.73 eV and 164.08 eV, characteristic of Bi in the +3-oxidation state, aligning with the expected chemical environment in Cs₂AgBiBr₆. The Br 3d core levels display Br $3d_{5/2}$ and Br $3d_{3/2}$ peaks at 68.03 eV and 69.08 eV as
shown in Figure 3.15(f), confirming the presence of Br in the double perovskite structure. These binding energy values are in agreement with those reported in the literature, supporting the successful formation of the Cs₂AgBiBr₆ perovskite film on the TiO₂ layer. The analysis of the Ti 2p core levels show Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks at 458.68 eV and 465.18 eV, respectively in Figure 3.15(g). Despite the noisy signal due to the underlying TiO₂ layer, these values confirm that titanium remains in the +4 oxidation state, characteristic of TiO₂. Figure 3.15(h) depicts the O 1s spectrum which reveals two peaks: one at 529.58 eV, attributed to lattice oxygen (O²⁻) in TiO₂, and another at 531.83 eV, associated with surface hydroxyl groups (OH⁻). Overall, the XPS analysis confirms the elemental composition and chemical states of Cs, Ag, Bi, and Br in the Cs₂AgBiBr₆ coating, as well as the integrity of the TiO₂ layer. These findings verify the successful coating of the double perovskite on TiO₂. The detailed binding energy values and chemical state information are crucial for understanding the material's properties and potential applications in PV devices.

3.3.5. AFM analysis of Cs2AgBiBr6 films



Figure 3.16 AFM data of Cs₂AgBiBr₆ film (**a**) topography image, (**b**) line profile analysis, (**c**) 3D AFM image, and (**d**) R_a and R_q roughness analysis.

The AFM topography image **Figure 3.16(a)** reveals a smooth surface morphology with nanoscale grains and height variations up to 51 nm, indicating low surface roughness, which is beneficial for solar cell applications. **Figure 3.16(b)** presents the line profile analysis of the AFM image, where the red curve illustrates minor height fluctuations along a selected line, corresponding to the surface grains. This smooth surface is advantageous for uniform light absorption and reduced scattering losses. **Figure 3.16(c)** provides a 3D AFM image, offering a detailed perspective on the surface topography. The 3D visualization confirms the presence of relatively smooth grains and shallow valleys, with heights reaching up to 51 nm. The roughness analysis shows **Figure 3.16(d)** a R_a of approximately 1.08 nm and a R_q of approximately 1.3 nm. The smooth surface morphology is crucial for enhancing the

uniformity of the thin film, leading to more consistent light absorption. This uniform absorption is essential for maximizing solar cell efficiency, minimizing scattering losses, and ensuring that more sunlight is converted into electrical energy. The polycrystalline nature of the film, indicated by the grain structures, supports efficient charge transport by reducing the density of grain boundaries, which are sites for charge carrier recombination. The low roughness values suggest a well-controlled film deposition process, resulting in high-quality thin films with excellent optical and electronic properties.

3.4. Investigation of CuSCN layer

Earlier research on $Cs_2AgBiBr_6$ double PSCs mainly concentrated on the use of spiro-OMeTAD as the hole-transporting layer and gold as the metal contact. Spiro-OMeTAD is an expensive smallmolecule organic material that needs precisely controlled hygroscopic dopants for optimal performance. In this study, low-cost, dopant-free CuSCN was employed as the HTL. Various methods, such as FESEM, XRD, and XPS, were used for characterization.

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3.4.1. XRD pattern of CuSCN layer

Figure 3.16 XRD pattern of CuSCN film coated on Cs₂AgBiBr₆ Film.

The XRD pattern depicted in **Figure 3.16** corresponds well with the rhombohedral crystal structure, matching with JCPDS card no. 29-0581. The distinct peaks observed at 20 angles of 16.15° , 27.18° , 31.98° , 34.48° , 47.12° , 50.02° , 55.21° , 57.92° , 59.63° , 62.38° , 68.84° , and 75.39° are attributed to scattering from specific crystal planes of CuSCN, including (003), (101), (006), (104), (110), (009), (021), (116), (024), (205), (027), and (211) respectively, with no impurity peaks

detected. The sharpness of these peaks indicates the good crystallinity of the deposited CuSCN layer.



3.4.2. FESEM images of CuSCN layer

Figure 3.17 FESEM images of the CuSCN film coated on Cs₂AgBiBr₆ absorber layer.

To check the CuSCN layer film coverage and morphology, we have performed FESEM of sample, and their results are depicted in **Figure 3.17**. shows CuSCN film coated on the $Cs_2AgBiBr_6$ film has a smooth surface with uniform coverage which is beneficial for the effective transport of charges from the absorber layer.

3.4.3. XPS analysis of CuSCN

The XPS analysis of CuSCN shows the elemental composition and chemical states. The survey spectra, as shown in **Figure 3.18(a)**, confirm the presence of Cu, S, C, and N within the samples. The carbon C 1*s* high-resolution spectra, depicted in **Figure 3.18(b)**, reveal distinct peaks that correspond to the bonding environments within the material. A peak at 285.4 eV is attributed to the S–C–N bonding configuration, demonstrating the interaction among these elements. Additionally, the presence of adventitious carbon is indicated by a peak at 284.4 eV, which serves as a calibration reference, ensuring the accuracy of the spectral data. Another notable peak at 288.5 eV suggests the presence of carbonyl (C=O), highlighting surface groups the potential contamination or functional groups within the sample. Further detailing the sulfur environment, the S 2p core level spectra present in Figure **3.18(b)** show a dominant peak at approximately 162.5 eV, assigned to the S $2p_{3/2}$ state, which indicates the typical oxidation state of sulfur linked with carbon and nitrogen. An additional peak at 164.2 eV, corresponding to the S $2p_{1/2}$ state, reinforces the presence of C-S bonding, essential for understanding the sulfur environment in CuSCN. The Cu 2p core level spectra, illustrated in Figure 3.18(c), exhibit significant peaks at 932.4 eV for Cu $2p_{3/2}$ and at 951.8 eV for Cu $2p_{1/2}$, suggesting the presence of Cu⁺ oxidation state. This is crucial for confirming the valence state of copper, which plays a important role in the electronic structure and properties of CuSCN. Lastly, the N 1s core level spectra, as indicated in the data, show a peak at 397.2 eV, which is consistent with nitrogen involved in S-C-N bonding, corroborated by the corresponding peaks in the C 1s and S 2p spectra. An additional peak at 399.5 eV further suggests the presence of C–N bonding, essential for verifying the chemical environment of nitrogen within the samples.



Figure 3.18 (a) Survey scan of CuSCN, high-resolution scans of (b) C1s, (c) S 2p, (d) Cu 2p, and (e) N 1s.

3.5. PCE

Above section completes the materials and device fabrication of TiO₂/Cs₂AgBiBr₆/CuSCN. Au is replaced with Ag as the metal contact, resulting in device configuration FTO/cа of TiO₂/TiO₂/Cs₂AgBiBr₆/CuSCN/Ag. Silver contacts were made on TiO₂ and top CuSCN to extract the electrons and holes generated after exposing the device to light. The devices were prepared by using the absorber layers Cs₂AgBiBr₆, heated at various temperatures of 200 to 300 °C. Evaluated the PV results of the best devices processed at five different temperatures: 200°C (Cell 1), 225°C (Cell 2), 250°C (Cell 3), and 275°C (Cell 4), the film processed at 300°C did not exhibit any PV behavior and hence excluded from the graph.



Figure 3.19 (**a**) fabricated Device structure for testing, (**b**) Cross-section FESEM image of device, and (**c**) Effect of temperature over solar cell parameters.

A typical cross-sectional device structure is illustrated in **Figure 3.19(a)** while cross cross-sectional image of the best-performing device is shown in **Figure 3.19(b)**. These findings indicate that the processing temperature of $Cs_2AgBiBr_6$ significantly impacts photovoltaic performance as shown in **Figure 3.19(c)**. These results are detailed in **Table 2**. Devices treated at 275°C demonstrated the highest PCE of approximately 1.75%.

Table	e 3.1	Solar	Cell	performance	of	devices	heated	at	different
tempe	ratur	es.							

Device	V _{oc}	J _{sc}	FF	PCE %
	(mV)	(µA/cm ²)		
FTO/c-TiO ₂ /TiO ₂ /Cs ₂ AgBiBr ₆	0	0	0	0
(300°C)/CuSCN /Ag				
FTO/c-TiO ₂ /TiO ₂ /Cs ₂ AgBiBr ₆	373.55	757.54	0.62	1.75
(275°C)/CuSCN /Ag				
FTO/c-TiO ₂ /TiO ₂ /Cs ₂ AgBiBr ₆	479.62	922.24	0.31	1.36
(250°C)/CuSCN /Ag				
FTO/c-TiO ₂ /TiO ₂ /Cs ₂ AgBiBr ₆	589.51	624.09	0.44	0.94
(225°C)/CuSCN /Ag				
FTO/c-TiO ₂ /TiO ₂ /Cs ₂ AgBiBr ₆	579.93	335.18	0.43	0.43
(200°C)/CuSCN /Ag				

The findings of this study highlight the potential of Cs₂AgBiBr₆ as a viable Pb-free alternative for PSCs. The improvement in film quality and device performance through optimized thermal treatment offers a pathway to overcoming some of the inherent challenges associated with double perovskite materials, such as poor stability and lower efficiency. The successful use of cost-effective materials like CuSCN as HTL and silver as contact material, further draws attention to the feasibility of developing economically viable and environmentally friendly PSCs.

	J _{sc}	Voc		PCE	
Device Structure	(mA/cm ²)	(V)	FF%	%	Ref
FTO/BL-TiO ₂ /mp-TiO ₂ layer/ Cs ₂ AgBiBr ₆ /					
Spiro-OMeTAD/Au	2.83	0.94	43.9	1.16	[70]
FTO/TiO2/C60/Cs2AgBiBr6/PCDTFBT/Au	2.25	1.01	69.3	1.57	[71]
ITO/TiO ₂ /Cs ₂ AgBiBr ₆ /Spiro-OMeTAD/					
Au	1.7	1.06	74	1.22	[72]
FTO/c-TiO ₂ /m-TiO ₂ /Li ⁺ -					
Cs2AgBiBr6/Carbon	3.15	1.177	69.4	2.57	[73]
FTO/c-TiO ₂ /m-TiO ₂ /Cs ₂ AgBiBr ₆ /Spiro					
OMeTAD /Au	2.1	1.02	64	1.4	[74]
FTO/TiO ₂ /Cs ₂ AgBiBr ₆ /spiro-					
OMeTAD/MoO ₃ /Ag	0.1	0.65	38.4	0.28	[75]
FTO/TiO ₂ /Cs ₂ AgBiBr ₆ /Spiro-					
OMeTAD/MoO ₃ /Ag	3.82	1.01	65	2.51	[76]
FTO/TiO2/Cs2AgBiBr6/Spiro-					
OMeTAD/Ag	3.93	0.98	63	2.43	[77]
FTO/c-					
TiO2/TiO2/Cs2AgBiBr6(275°C)/CuSCN	0.754	0.32	62	1.75	Present
/Ag					work

 Table 3. 2 Comparison of double perovskite performances.

From **Table 3.3** it is concluded that the devices either fabricated in an inert controlled atmosphere and or using Spiro-OMeTAD/MoO₃, PCDTFBT, *etc* expensive HTL delivered about 0.75 % higher efficiency. However, in the present study, the devices were fabricated in open atmospheres and used CuSCN as HTL, but still delivered an efficiency of 1.75 %, which is comparable with this literature and compatible. Hence this work is very important.

In summary, the double perovskite Cs₂AgBiBr₆ material was successfully synthesized at ambient conditions at different annealing temperatures which affects the performance of the device achieving the efficiency of 1.75 eV. This is the first report on FTO/c- $TiO_2/TiO_2/Cs_2AgBiBr_6/CuSCN/Ag$, no report was found as per my knowledge to date. Merits of this study is that we used CuSCN as HTL which is much cheaper than traditional HTL. Expensive Au is replaced by Ag.

Chapter 4

Discussion and Future prospects

This study investigates the influence of temperature variations on the synthesis and performance of Pb-free Cs₂AgBiBr₆-based double PSCs. The primary aim was to enhance the PCE of these cells through achieving optimal film quality via precise temperature control. Cs₂AgBiBr₆ thin films were synthesized using a spin-coating method in ambient air and annealed at temperatures ranging from 200°C to 300°C. The optimal temperature for producing phase-pure films with high crystallinity and minimal defects was determined to be 275°C. Films annealed at this temperature exhibited smooth, uniform surfaces essential for enhanced carrier transport. The best-performing PSCs, which utilized CuSCN as the HTL and silver contacts, achieved a PCE of 1.75%. Although this efficiency is lower than that of Pb-based counterparts, it represents a significant improvement for LFPSCs and shows enhanced atmospheric stability, crucial for practical applications.

Cs₂AgBiBr₆ has emerged from recent studies as a promising Pbfree double-halide perovskite for use in PSCs. Its appeal lies in its outstanding structural, photoemission, and physical properties, coupled with its non-toxic and stable characteristics. However, the PCE of Cs₂AgBiBr₆PSCs has generally been lower compared to traditional Pbbased PSCs, primarily due to intrinsic and extrinsic defects in the material.

In comparison, our study employed CuSCN as the HTL and Ag contacts, marking a novel approach compared to the conventional use of Spiro-OMeTAD and gold. Despite these cost-effective and simpler fabrication methods, our devices achieved a PCE of 1.75%, which is competitive with other $Cs_2AgBiBr_6$ PSCs and demonstrates improved atmospheric stability.

Numerous studies have explored various methods of fabricating Cs₂AgBiBr₆PSCs, achieving efficiencies ranging from as low as 0.08% to as high as 6.34% under different device configurations and synthesis

techniques. Our research utilized ambient condition (open-air) synthesis of $Cs_2AgBiBr_6$ films, a challenging method compared to the controlled environments, such as glove boxes, used in other studies. This approach aimed to simplify the fabrication process and reduce costs, although it posed challenges in achieving high-quality films. The systematic investigation of annealing temperatures revealed that 275°C was optimal for achieving phase-pure films with high crystallinity. This temperature facilitated the formation of smooth, uniform surfaces, which are crucial for efficient carrier transport.

Most studies have utilized Spiro-OMeTAD as the HTL, a costly small-molecular organic material requiring precisely controlled hygroscopic dopants to optimize its performance. Other studies have explored different HTLs, such as PEDOT: PSS, CuSCN, Cu₂O, and NiO, with varying degrees of success. Au is frequently used as a metal contact due to its high conductivity and stability, although it significantly increases the cost of the devices. In our study, we used CuSCN as the HTL, an approach not extensively explored in previous Cs₂AgBiBr₆ PSC studies beyond simulation. CuSCN is a low-cost, dopant-free alternative to Spiro-OMeTAD, offering a simpler fabrication process while still achieving comparable efficiency.

Our findings underscore several important implications for the field of LFPSCs. The enhanced atmospheric stability of $Cs_2AgBiBr_6$ PSCs positions these cells as viable candidates for real-world applications, addressing a major drawback of many perovskite materials. Moreover, the use of CuSCN as an HTL and Ag contacts demonstrates the potential for reducing the cost of PSC fabrication without significantly compromising efficiency. The identification of 275°C as the optimal annealing temperature provides valuable insight into the processing conditions necessary for synthesis of high-quality $Cs_2AgBiBr_6$ films.

While our study presents significant advancements, certain limitations must be acknowledged. The PCE of 1.75% is still lower than

Pb-based PSCs, indicating a need for further optimization and exploration of alternative materials and structures.

Based on our findings, future research could focus on advanced characterization techniques to further understand and mitigate efficiency-limiting factors such as defect states and carrier dynamics in Cs₂AgBiBr₆ films. Exploring other low-cost, efficient HTLs and ETLs could also contribute to improved device performance. Conducting long-term stability studies under various environmental conditions would validate the real-world applicability of these PSCs.

By addressing these aspects, future work can build on our results to develop more efficient, stable, and cost-effective Pb-free PSCs. Still, there is room to improve the efficiency of this type of device by preparing it under controlled conditions like an inert atmosphere which will help to enhance the efficiency. The stability test of the device is still lacking and can be studied. The encapsulation of the device is another issue to be addressed. To check the working temperature/weather conditions over years is another aspect of the study that needs to be addressed.

List of Publications

First Author

1. Shaikh Azaharuddin Saleem, Subhash Chand Yadav, Abhishek Srivastava, Archana R. Kanwade, Manish Kumar Tiwari, Shraddha Manohar Rajore, Jena Akash Kumar Satrughna, Mahesh Dhonde, and Parasharam M. Shirage* "The Dynamic Synergy of Tin in Electron Transfer Layer and Absorber Layer for Advancing Perovskite Solar Cells: A Comprehensive Review", *Energy Advances* (**Publsihed**) DOI:10.1039/D4YA00204K.

2. Shaikh Azaharuddin Saleem, and Parasharam M. Shirage* "Effect of synthesis temperature on photoconversion efficiency of double perovskite Cs₂AgBiBr₆ solar cells", (Under Preparation 2024).

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