

PAPER 92 – A HOLISTIC APPROACH TOWARDS MODELLING, SYNTHESIS AND FABRICATION OF ORGANO-INORGANIC PEROVSKITE SOLAR CELL MODULE

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ABSTRACT

The quest in searching for new material(s) for harvesting abundant solar energy in our society lead to the discovery of a perovskite family which possesses a photovoltaic effect. Halide perovskite solar cells (HPSCs) have become the next-generation solar technology due to their outstanding characteristics. Despite considerable improvements in the HPSCs' efficiency, there have been concerns about the conceptualization of the holistic approach involved in creating PSC modules from scratch. The overall performance of the OIHP solar cell module significantly relies on the material composition of the thin layers making up the module, their synthesis techniques, and the fabrication method employed. This paper provides a pathway for modelling, synthesis, and fabrication of solar cell module. The paper emphasized on modelling of chemical compositions of the light-absorbing layer using Goldsmith factors, synthesis techniques, device architectural configuration, and method of fabrication. Hence this review serves as a guide to a novice in the field of solar cell research in generating PSC modules from scratch.

KEYWORDS: Perovskite, Photovoltaic, Synthesis, fabrication, Goldsmith.

1.0 INTRODUCTION

1.1 Background of Study

A variety of scientific innovations, including solar power to produce electricity, solar thermal energy, and solar architecture, are employed to capture the radiant light and heat from the Sun. Solar energy, which is clean and reduces environmental pollution, can be used to generate a considerable amount of the energy required by human society. This will help to slow down the effects of climate change and global warming. There is a growing understanding that fossil fuel sources are rapidly depleting, or that they are not sustainable from an economic or environmental standpoint. The exponential growth of installed capacity for renewable energy power plants using sources like the sun and wind is self-sustaining due to constantly expanding economies of scale and supply chains, as well as a better understanding of the fundamental properties needed for both economical and efficient solar energy converters [1-3]. Kojima et al discovered in 2009 that the organic metal halide perovskite was comparable to dyes and could absorb sunlight. He claims that a liquid electrolyte and perovskite can be used in dye-sensitized solar cells to obtain a power conversion efficiency (PCE) of 3.8% [4]. A solid-state perovskite solar cell with a PCE of 9.7% was initially reported by Kim et al. in 2012 [5]. Perovskite solar cells have garnered the interest of numerous researchers worldwide in recent years due to their high efficiency and low cost. The amount of research published on this topic as well as the reported efficiencies have risen dramatically since the initial reports on solid-state perovskite solar cells with an efficiency of 10% in 2012 [5,6]. According to NREL, certified record efficiency now exceeds 22%. It is obvious that the perovskite solar cells (PSCs) record efficiency of 22.1% already outperform some of the well-established technologies, such as amorphous Si (13.6%), thin film and multi-crystalline Si (21.2% and 21.3%, respectively), and they are comparable to CdTe (22.1%) and CIGS cells (22.3%). Despite considerable improvements in the perovskite solar efficiency, there have been major concerns about the conceptualization of the holistic steps involve in generating PSC modules from scratch. This paper is focused in provide an overview of the modelling of PSC materials, synthesis and characterization of the PSC layers, device architectural configuration, and the method of fabrication. This review will hence provide a summary of practical details needed to pay attention to in developing, synthesis, and fabricating of PSC module.

2.0 METHODS AND MATERIALS

2.1 Modelling

Perovskite structure has an empirical formula ABX_3 . The A and B-site are normally occupied with cation of different sizes such that $A > B$. For Organo-Inorganic halide perovskite, A- site is normally occupied with organic mono-cation and B-site occupied with divalent cation while X-site is occupied with halide ion as shown in Fig2.1.

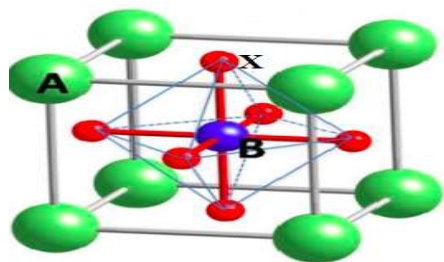


Fig 2.1: Crystal structure of a typical perovskite structure [7]

2.1.1 Structural Stability Modelling for Perovskite cluster

The first thing to do after conceiving the idea of generating a solar cell module from Organo-Inorganic Halid Perovskite (OIHP) is to carefully select the organic mono-cation, the divalent cation, and the appropriate halide anion. Many cations and anions have been modelled for this purpose as illustrated in Table 2.1. After this, the next is to model for stability of the structure using Goldsmith factors given in Equations 1, 2, 3, and 4. However, many theoretical modellings are used toward improving the efficiency of OIHP cluster which include viz; First principle density function model, Equivalent circuit model, Atomistic model, Opto-electronic modelling.

Table 2.1 Calculated effective ionic radii of A-organic cations, metal cations and halide anions [8,9]

A-Cation	$r_{A,eff}$	B-Cation	$r_{B,eff}$	B-Cation	$r_{B,eff}$	X-Anion	$r_{X,eff}$
Ammonium $[NH_4]^+$	146	Be^{2+}	45	Ag^+	115	I^-	220
Hydroxylammonium $[NH_3OH]^+$	216	Mg^{2+}	72	Cd^{2+}	95	Br^-	196
Methylammonium $[CH_3NH_3]^+$	217	Ca^{2+}	100	Ba^{2+}	135	Cl^-	181
Hydrazinium $[NH_3NH_2]^+$	217	Ti^{2+}	86	Eu^{2+}	117	F^-	133
Azetidinium $[(CH_2)_2NH_2]^+$	250	V^{2+}	79	Tm^{2+}	103		
Formamidinium $[CH(NH_2)_2]^+$	253	Cr^{2+}	80	Yb^{2+}	102		
Imidazoline $[C_3N_2H_5]^+$	258	Mn^{2+}	83	Pt^{2+}	80		
Ethylammonium $[CH_3CH_2NH_3]^+$	274	Fe^{2+}	78	Hg^{2+}	102		
Guanidinium $[(NH_2)_3C]^+$	278	Ni^{2+}	69	Np^{2+}	110		
Tetramethylammonium $[(CH_3)_4N]^+$	292	Cu^+	77	Ni^{2+}	69		
Thiazolium $[C_3H_4N_5]^+$	320	Cu^{2+}	73	Sn^{2+}	115		
3-pyrrolinium $[NC_4H_8]^+$	272	Zn^{2+}	74	Sb^{3+}	76		
Tropylium $[C_7H_7]^+$	333	Ge^{2+}	73				
Cesium $[Cs]^+$	167	Sr^{2+}	118				
Potassium $[K]^+$	138	Ag^{2+}	94				

The Goldschmidt Tolerance (GT) factor was used to determine the structural stability of perovskites. The GT factor (t) of ABX_3 is expressed in Equation (1), and the tolerance factor is given by

$$t = (1)$$

where r_A is the ionic radius of the A-cation, r_B is the ionic radius of the B-cation, and r_X is the ionic radius of the X-anion. The ideal cubic structure of the tolerance factor, t, is often between 0.9 and 1.0. A non-perovskite structure developed when the tolerance factor, t, was less than 0.71 or larger than 1.0 [10]. When $t > 1$, the A-

cation is fairly large, which could perhaps lead to the creation of non-perovskite. Conversely, when $t < 0.8$, the A-cation is very little, which could potentially develop non-perovskite structure. Perovskite structures can often occur in the range of 0.8 to 1.0. A tolerance factor limit of 1.06 – 1.07 is considered for OIHP [11]. GT factor is unable to accurately forecast the ionic radius of organic cations in hybrid perovskite because of hydrogen bonds. Cheetham and colleagues used the rigid sphere model for organic cations, presupposed rotational freedom, and expanded the Goldschmidt Tolerance Factor equation to solve this difficulty is given in Equation (2).

$t = (2)$

r_{Aeff} is given as $r_{mass} + r_{ion}$ [8].

According to reports, relatively few perovskite-type oxides exhibit an ideal cubic structure at ambient temperature, but many do so at higher temperatures.

However, an extended tolerance factor given by Equation (3) indicates the formability of the perovskite structure.

$\tau = (3)$

where n_A is the oxidation state of A, r_X is the ionic radius of ion X, $r_A > r_B$ by definition and

$\tau < 4.18$ indicates perovskite.

For stability of the structure, the octahedra factor which is defined as the ratio of the ionic radii of the B cation and the halide anion is given in Equation (4).

$\mu =$

This indicates the stability of the BX_6 octahedron and it is limited within the range of 0.44 for a stable perovskite.

For example, to model $CH_3NH_2PbI_3$ cluster, the ionic radii of the constituent elements of the site A, B and X are needed. Here A site is occupied with CH_3NH_3 with ionic radius of 2.17\AA . B-site is occupied with Pb with ionic radius of 1.19\AA and ionic radius of I in X-site is 2.2\AA

cluster in accordance with the Equation (2), the tolerance factor, $t = 0.912$

Which means the formation of $CH_3NH_2PbI_3$ is possible and it is within the tolerance factor for organic halide perovskite. Using the extended tolerance formula given in the Equation (3),

with $n_A = 1$, $\tau = 3.88$ which is less than 4.18. This indicates that the structure chosen is a perovskite.

For stability of the structure, octahedra factor given in Equation (4) for $CH_3NH_2PbI_3$, μ is equal to 0.54 which is within the limit of stability of perovskite.

2.2 Selection of Synthesis Techniques

Chemical synthesis involves the artificial carrying out of necessary chemical reactions to produce one or more products [9]. Highlighted below are some of the most common techniques used for synthesizing perovskite materials;

Temperature-lowering crystallization: This includes the formation of crystals from a solution. It is a suitable approach for the crystal formation of hybrid-halide perovskites, whose temperature-dependent solubility in the associated acid halide solvents is mild at room temperature. The seed is inserted into the solvent to create high-quality single crystals, and crystal development occurs on the seed when the solution temperature is lowered. The precursor becomes saturated when the solution temperature is lowered. The method of solution growth with slow cooling is the most recommended, but it needs to be used with a range of temperatures. To counter this effect, a high volume of solution is needed because the allowable temperature range is often small and leaves a significant amount of the solute in the solution at the end of the growth run. A programmable temperature controller is also necessary [10].

The saturated solution must be kept at a chosen temperature and space must be made for evaporation to use the slow evaporation method. The reaction must be stabilized at a temperature of about 0.05°C and evaporation rates of just a few mm^3/h . A limitation on the crystal development rate, however, is fluctuations within the small temperature differential between the reactants and the crystal zones [11].

Inverse temperature crystallization: Inverse temperature crystallization (ITC) method is used for synthesizing perovskites whose solubility is lost at an elevated temperature in a particular solvent, which favours their crystallization at elevated temperature. Most solids solubility increases as their temperature is elevated and hence, their crystallization is normally performed by lowering the temperature of the solution. To grow one crystal of organo-halide perovskite $CH_3NH_2PbI_3$ crystal using ITC, a calculated mass of CH_3NH_2PbI and PbI_2 is added to a glass vial that has been properly mixed with 5ml of Gamma-GBL. To completely dissolve the resulting combination, it is heated in an oil bath to 60°C . The perovskite solution is then heated for two hours at 152°C in an oil bath. After heating, the crystal will form and be filtered through a chosen Polytetrafluoroethylene (PTFE) filter with the required pore size. The temperature must be adjusted between 150 and 160°C because crystal growth is small and irregular at temperatures below 150°C and massive but irregular at temperatures over 160°C . Therefore, 152°C is the optimum and recommended temperature for growing a big, regular crystal. The benefit of this procedure is that crystallization can take place in the shortest possible (2- 3 h)

Ant-solvent vapour assisted crystallization: Anti-Solvent Assisted Inverse Temperature Crystallization is used for synthesizing a perovskite whose When a compound's concentration surpasses its solubility, precipitation in a

solution happens quickly. Gradual lowering of the temperature of the solution will bring about Super-saturation. Conventionally, as heat is added to a system, its solubility increases (Some perovskites-in-solvent systems are an exception to this rule) [12]. As a result, more solute can dissolve at high temperatures than at room temperature. This solution will become supersaturated if it is abruptly cooled at a rate faster than the rate of precipitation until the solute precipitates to the temperature-determined saturation point.

Solvent evaporation crystallization: When the concentration is increased to reach saturation, solvent evaporation may be a conventional approach to start crystallization. It takes a lot of time and is difficult to correctly control [13, 14]. Recently, Huang et al [13] reportedly used the solvent evaporation crystallization approach at higher temperatures (80°C) to synthesize a single-crystal perovskite thin film with the formula $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ ($\text{FA}=\text{CH}(\text{NH}_2)^{2+}$). Such single-crystal perovskite thin films have lateral diameters ranging from 500 nm to 2 mm and micrometre-scale thicknesses (10–50 nm).

Hydrothermal Synthesis: Hydrothermal synthesis is a technique for creating crystals that relies on a substance's solubility in extremely hot water while under pressure. It entails selecting the reaction reagent as the first ingredient. Potassium hydroxide (KOH) or sodium hydroxide (NaOH) are frequently used as mineralizers. The chosen reaction reagents will be dissolved in deionized water to create a solution; KOH or NaOH will then be added to the resulting solution and will be agitated to control the solution's alkalinity. The initial reagent mole ratios will be chosen stoichiometrically. After being vigorously mixed, the reaction mixture will be placed into a Teflon vessel until 80% of its volume has been filled. For hydrothermal treatment operations, the vessel is often housed in a stainless-steel tank. Depending on the recipe, it is necessary to manage the crystallization temperature and time.

Device Architectural Configuration: Perovskite solar cells are still improving, which remarkably gives rise to the creation of new materials for usage in cells and the most current attempts to understand how perovskite devices function. The final product's electrical and optical characteristics are significantly influenced by the perovskite solar cell's overall architecture and material selection. The transparent conductive oxide (TCO) layer, the electron-transporting layer (ETL), the light-harvesting perovskite material, the hole-transporting layer (HTL), and the metal contact material are the five groups into which the materials used in perovskite solar cells can be categorized as shown in Fig 2.2

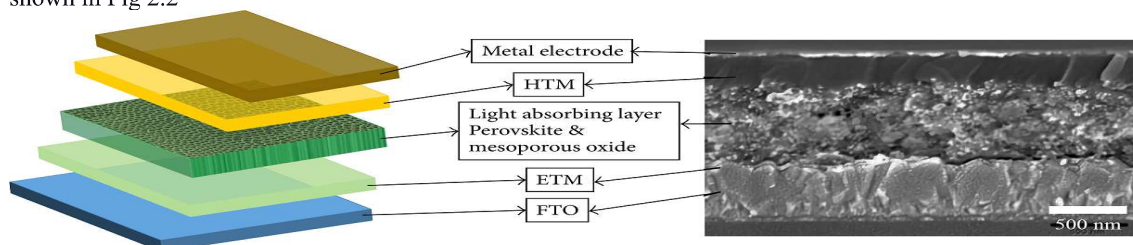


Fig 2.2 Typical SEM view of solar cell module [15]

There are two types of architectural configurations for solar cell modules. These include regular n-i-p and inverted p-i-n configurations.

Generally, the architecture of PSCs can be categorized as direct (n-i-p) and inverted (p-i-n) with either planar or mesoscopic structures, as depicted in Fig 2.3. The mesoscopic structure mainly contains a mesoscopic oxide scaffold, including titanium dioxide (TiO_2), which has been reported to obtain high device PCE [16] which is strongly related to the thickness of TiO_2 typically in the range 300-1000 nm.³³ However, the mesoscopic oxide often needs high heat treatment [17, 18] which harms device performance and limits the industrial manufacturing roll-to-roll process toward the implementation of flexible devices. Hence, researchers are interested in exploring PSCs with planar structures, especially in inverted architecture. Inverted planar PSCs is a promising device as it offers excellent advantages such as owing low-temperature procedures that are compatible with large-scale production and suitable for flexible and wearable devices [19]

For the direct (n-i-p) architecture, the electron transport material (ETM) is fabricated above transparent conductive oxides (TCO) such as fluorine-doped tin oxide (FTO) or indium tin oxide (ITO) followed by perovskite layer, hole transport material (HTM), and top contact electrode. Meanwhile, in the inverted (p-i-n) configuration, HTM is deposited onto the TCO while ETM is layered onto the perovskite material before implementing the top contact electrode. The energy alignment is crucial in order to follow the device architecture, for instance, the conduction band (CB) of the electron transport layer (ETL) should be closer to that of perovskite in order to accept the photogenerated electron and the CB should be matched with top electrode for inverted device architecture whereby the CB of ETL should be matched with TCO for direct device architecture for efficient electron transport [20]

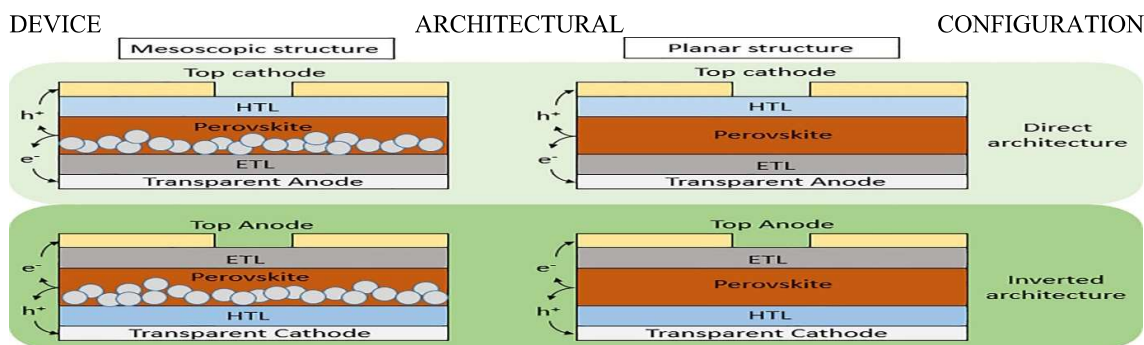


Fig 2.3 Schematic showing the device architecture of perovskite solar cells [21]

2.4 Fabrication Methods of Perovskite Solar Cell

Various deposition techniques have been employed in the fabrication of hybrid perovskite solar cells. The method for depositing perovskite thin films that uses solution processing is the most popular. Solution processing methods. Spin Coating: Spin coating is commonly used in the fabrication of organic-inorganic perovskite due to its low cost and easy processing. This is mainly for producing small-area solar cells at the research laboratory level. In this method, a small puddle of a solution is first deposited onto the centre of a substrate to fully cover the substrate and eventually spun to accelerate the evaporation of the solvent [22]. The substrate is accelerated to the final rotation speeds range from 500 – 10000 rpm. The rotation of the substrate at high-speed means that the centripetal force combined with the surface tension of the solution pulls the liquid coating into an even covering. During this time the solvent then evaporates to leave the desired material on the substrate in an even covering. The method could be further classified into; one-step deposition and two-step deposition methods. In the one-step deposition method, all the precursors of the perovskite (either in 1:1 stoichiometry or 3:1 non-stoichiometry ratio) are dissolved in a common solvent (such as DMF, DMSO, GBL, etc) in the same solution. In the two-step deposition method, a precursor of the metal halide is first deposited onto the prepared substrate usually by spin coating, and annealed to evaporate all the residual solvents. Then follow by dipping the coated substrate (at room temperature) into ammonium iodide solution (for a short period suitably 15 min) for the formation of the corresponding organic-inorganic halide perovskite layer. When the desired dipping time passed, the slide is subjected to annealing to evaporate the solvent. Two-step deposition provides better morphology control over one-step deposition [23].

Spray Coating: Spray coating is a productive solution-based method for making solar cells. Due to the liquid atomization effect, which results in a random spray of droplets of various sizes and increases series resistance, it is rarely reported [24]. The spray coating parameters; film drying time, substrate temperature, solvent engineering, and post-annealing conditions are required to be controlled to achieve high coverage perovskite films [18]. Spray coating expresses the advantage of producing solar cells on a large scale in contrast to spin coating which a thin film solar cell on a small-area thin film is fabricated in research laboratories.

Blade Coating Method: Using a blade coater applicator is one of the simplest, most eco-friendly, vacuum-free, and cost-effective solution-processed ways of manufacturing PSC on an industrial scale. The blade coater applicator is a conventional coating method that consists of a micrometer-sized screw used to control the blade's height with respect to the substrate surface [25]. In this method, airflow over the substrate can be modified to control the rate at which inks evaporate or the substrate can be heated to the solvent's boiling point to manage film uniformity and quality. Compared to spray coating and other roll-to-roll compatible methods, this process provides superior control over film shape. The manufacture of planar heterojunction PSCs is done using this method. Due to non-uniform deposition and the presence of moisture and air, the majority of perovskite deposition procedures typically cause pinhole formation in the perovskite layers, which frequently reduces the performance of solar systems. Blade coating is recommended as a means of overcoming these difficulties [26]. For the creation of self-assembled perovskite crystalline domains with features like homogeneous film coverage and enhanced device stability, it is one of the highly identified strategies. Additionally, the ease of application on flexible substrates and uniform, high-throughput deposition are benefits of this approach [27].

Screen Printing: Screen printing is a simple and promising technique for producing solar cells. In this method, a mesh with a desired printing design is placed over the substrate on which printing is designed. The mesh is pressed with the help of a moving blade or squeegee. The process starts with the printing of TiO₂ (electron transporting layer) followed by the printing of ZrO₂ (spacer layer) and carbon black/graphite top electrode. Then the perovskite solution is dropped onto the porous carbon electrode so that it infiltrates into the mesoporous TiO₂ and ZrO₂. The ZrO₂ as a porous insulating layer is used to prevent direct contact between the carbon electrode and the TiO₂/FTO substrate. The infiltration of the perovskite solution is the major challenge associated with this technique [28]. Slot-die Coating: The slot-die coating is a solution-processed method widely used for fabricating perovskite solar

cells. This method is almost similar to the blade-coating process but has the advantage of using less material. Slot-die coating resulted in poor film formation by the perovskite precursor solution and a two-step method is adopted to enhance good film formation. First, PbI_2 is applied using the slot-die coating. Then the PbI_2 was reacted with MAI solution and formed MAPbI_3 . Also, the continuous flow of nitrogen gas on the surface of the substrate during deposition assists in the formation of uniform film and controls the solvent evaporation rate, and ensures pin-hole free [26].

Brush Painting: Brushing painting is one of the simplest techniques for creating perovskite solar cells is brush painting. It is a low-material loss, high-speed fabrication method. Since there is no annealing process involved, it is a faster procedure. It is a very economical approach that may be applied to flexible solar cells with a wide surface area. A high-efficiency solar cell can be produced by properly optimizing the solvent and perovskite material concentrations. Furthermore, this method eliminates the necessity for experimental condition control and other time-consuming steps [28, 29]. The lack of a vacuum and quick processing are two benefits of brush painting, making it a particularly economical approach. Brush-painted devices are more efficient than spin-coated ones since thermal annealing is not necessary. The difficulty of maintaining a consistent thickness when painting using brushes.

Electrodeposition: PSCs are produced using the adaptable, roll-to-roll compatible technology of electrodeposition. It is a preferred method for perovskite layer deposition due to its efficiency, speed, and high level of homogeneity [30]. The substrate is not heated during this process, in contrast to spin-coating, because heating creates a rough layer. On the substrate's surface, film breakdown and island creation occur at random when heat is applied [31]. Electrodeposition creates highly uniform thin layers, covers a broad area, and lacks sheer forces [32, 33]. It is a particularly intriguing method for manufacturing at a large scale since perovskite layer deposition on complex-shaped substrates is conceivable with this method rather than the other ways we've mentioned so far [31].

3.0 CONCLUSION

Perovskite solar cells have advanced rapidly, however, there are certain substantial constraints that could limit their advancement. Firstly, external environmental conditions (such as humidity, temperature, and ultraviolet light) have a significant impact on the stability of organic lead halide perovskite, which results in low device stability and significant issues encasing cells later on. Therefore, to increase the viability of such devices, it will be essential to develop a high-stability device composition that incorporates the light-absorbing layer, electron/hole transport layer, and electrode materials, as well as an affordable and efficient device packaging method. The overall performance of the OIHP solar cell module significantly relies on the material composition of the individual layer making up the module, their synthesis techniques, and the fabrication method employed. This paper hence gives an overview of pathways followed in modelling, synthesizing, and fabrication of solar cell modules. The paper emphasized the selection of chemical compositions of the light-absorbing layer and it modelling using Goldsmith factors, synthesis techniques, device architectural configuration, and method of fabrication. Hence this review will serve as a guide to a novice in the field of solar cell research.

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