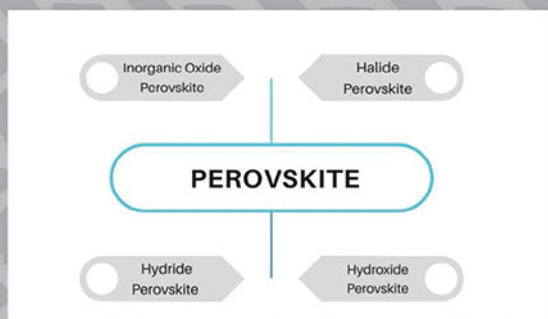


Perovskite based Materials for Energy Storage Devices



*Inamuddin, Maha Khan,
Mohammad Abu Jafar Mazumder*

MIRIF

Perovskite based Materials for Energy Storage Devices

Edited by

Inamuddin¹, Maha Khan¹, Mohammad Abu Jafar Mazumder^{2,3}

¹Department of Applied Chemistry, Zakir Husain College of Engineering and Technology,
Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202002, India

²Chemistry Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi
Arabia

³Interdisciplinary Research Center for Advanced Materials, King Fahd University of Petroleum
& Minerals, Dhahran 31261, Saudi Arabia

Copyright © 2023 by the authors

Published by **Materials Research Forum LLC**

Millersville, PA 17551, USA

All rights reserved. No part of the contents of this book may be reproduced or transmitted in any form or by any means without the written permission of the publisher.

Published as part of the book series

Materials Research Foundations

Volume 151 (2023)

ISSN 2471-8890 (Print)

ISSN 2471-8904 (Online)

Print ISBN 978-1-64490-272-1

eBook ISBN 978-1-64490-273-8

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify this in any future reprints.

Distributed worldwide by

Materials Research Forum LLC

105 Springdale Lane

Millersville, PA 17551

USA

<https://www.mrforum.com>

Manufactured in the United States of America

10 9 8 7 6 5 4 3 2 1

Table of Contents

Preface

Organic-Inorganic Perovskite Based Solar Cells

M. Rizwan, A. Ayub, S. Urossha, M.A. Salam, M.W. Yasin, A. Manzoor,
S. Mumtaz 1

Organometallic Halides-Based Perovskite Solar Cells

Uzma Hira, Muhammad Husnain 33

Perovskite Based Ferroelectric Materials for Energy Storage Devices

M. Rizwan, A. Ayub, T. Fatama, H. Hameed, Q. Ali, K. Aslam, T. Hashmi 67

Techniques for Recycling and Recovery of Perovskites Solar Cells

Somi Joshi, Kanchan Chaudhary, Kalpana Lodhi, Manjeet Singh Goyat,
Tejendra K. Gupta 89

Lead-Free Perovskite Solar Cells

Mridula Guin, Riya Singh 111

Technical Potential Evaluation of Inorganic Tin Perovskite Solar Cells

Lutfu Sagban Sua, Figen Balo 155

Keyword Index

About the Editors

Preface

In the third generation of photovoltaic systems, the invention of organic/inorganic-based hybrid perovskite materials has transformed the technology. The efficiency of perovskite materials for solar cells has increased almost by 22% in the last decade. There are several reasons for the power conversion efficiency (PCE's) strong optical absorption, balanced charge transfers, and thicker diffusion layer. The n-i-p and p-i-n with mesoporous or planar heterojunction perovskite solar cell architectures have emerged as the two most common types. Perovskite-based supercapacitors now have some of the desirable light harvesting features, such as higher absorption coefficients, longer carrier lifespans and diffusion lengths, bipolar transport of carrier, and superficial defect levels, thanks to the unending efforts to enhance perovskite solar cells. There have also been significant improvements in the cell architecture, working procedure, layer development, and bandgap correction of perovskite solar cells. This book overviews the reason for perovskite supercapacitors to be a commercially viable future power solution in the next few years due to their increased efficiency, cost-effective raw materials and processing, superior optoelectronic characteristics, and simple device construction procedures. The summaries of the chapters are given below:

Chapter 1 discusses the organic-inorganic perovskite solar cells (PSCs), their structure, and optoelectronic properties. The influence of individual and mixed substitution at A, B, and X sites on properties such as band gap and performance of these solar cells is also discussed. Various materials used for the electron transport layer, hole transport layer, and absorbing layer and their fabrication methods such as spin coating are discussed. Challenges and future perspectives are also discussed.

Chapter 2 throws light on modern trends in solar cells (SCs). The main theme of this content is on the organometallic halides-based perovskite solar cells (OMHP-SCs) and their structure, parameters, classification, and photovoltaic effect. Environmental instability, power conversion efficiency (PCE), and advancement through passivation techniques in OMHP-SCs are also discussed.

Chapter 3 discusses ferroelectric-based perovskites that are mainly used in storage devices such as capacitors, and fuel cells. Lead-based perovskites such as niobate and lanthanum-based ferroelectric perovskites are discussed. Lead-free perovskites such as barium titanate-based, bismuth-based, and alkaline niobate-based are also highlighted. Different energy storage devices and ways to improve their efficiency with methods like chemical substitution are discussed.

Chapter 4 discusses the roadmap and need for recycling perovskite-based solar cell modules, the toxicity behavior of lead present in the solar cells, and the recycling of

different parts of perovskite solar cells. It also sheds light on the cost analysis of recycling and future challenges.

Chapter 5 presents the current status of lead-free perovskite solar cells (PSCs) and their prospects. Various strategies to enhance photovoltaic efficiency are discussed in detail. Several materials are highlighted that can be explored further to progress in this area. Lastly, different fabrication processes of high-quality PSC film and associated challenges are discussed.

Chapter 6 analyses the most effective solar cell among the latest inorganic tin perovskite solar cells by AHP methodology. The inorganic tin perovskite photovoltaic cells as the selection problem with multiple-criteria decision-making methodology have been first examined by this research.

Chapter 1

Organic-Inorganic Perovskite Based Solar Cells

M. Rizwan^{1*}, A. Ayub², S. Urossha¹, M.A. Salam¹, M.W. Yasin¹, A. Manzoor¹, S. Mumtaz¹

¹School of Physical Sciences, University of the Punjab, Lahore, Pakistan

²Department of Physics, University of the Punjab, Lahore, Pakistan

*rizwan.sps@pu.edu.pk

Abstract

Traditional silicon-based solar cells have dominated the photovoltaic industry for quite some time now. Alternatives of these solar cells are being researched such as hybrid organic-inorganic perovskite-based solar cells, which are cost-effective and have the potential to achieve higher efficiency and performance. The characteristics of these perovskites can be controlled via substitution at A, B, or X sites since all these have a great impact on the overall performance. The components of perovskite solar cells (PSC) along with materials used for these layers, and fabrication techniques that give the optimized efficiency, challenges, and future perspective faced by perovskite solar cells are also deliberated.

Keywords

Lectron Transport Layer, Spin Coating, Organometallic Materials, One-Step Deposition Perovskites, Hole Transport Materials

Contents

Organic-Inorganic Perovskite Based Solar Cells.....	1
1. Introduction.....	3
2. Silicon Solar Cells (SSCs).....	5
3. Perovskites-Based Solar Cells (PSCs).....	6
3.1 Structure of PSCs.....	7
3.2 Optoelectronic Properties Of PSCs	9
3.3 Influence of A, B, and X site	10

3.3.1	A-Site.....	10
3.3.2	B-Site.....	10
3.3.3	X-Site.....	11
4.	Mixed Concentration of Perovskite Absorbing Layer.....	11
4.1	A-site.....	12
4.4	Mixed B-Sites Cations.....	13
4.5	X-Site.....	13
5.	Requirements for Each Layer.....	14
5.1	Electron Transport Layer.....	14
5.1.1	Different ETL Material Used In Perovskite Cells.....	15
5.2	Hole Transporting Layer.....	15
5.2.1	Hole Transporting Material (HTM).....	16
5.2.2	Inorganic P-type semiconductors as HTMs.....	16
5.2.3	Organometallic HTMs.....	17
5.3	Absorbing Layer.....	17
5.3.1	Preparation Method of The Perovskite Light Absorbing Layer.....	17
6.	Fabrication Techniques.....	18
6.1	One-Step Deposition.....	18
6.2	Two-Step Deposition.....	18
6.3	Vapor Deposition Method.....	20
6.4	Spin Coating.....	21
6.4.1	One-Step Spin Coating.....	21
6.4.2	Two-Step Spin Coating.....	21
6.5	Thermal Vapor Deposition.....	21
7.	Challenges in Perovskite-Based Solar Cells.....	22
7.1	Stability Challenges.....	22
7.2	Thermal Effect.....	23
7.3	Toxicity.....	23
7.4	J-V Hysteresis.....	24
8.	Efficiency of Perovskite.....	24

9. Future Perspectives26
Conclusion.....26
References27

1. Introduction

The energy crisis has caused dire consequences for the world economy. With time, energy needs have become the biggest problem because of the increase in demands day by day. The cheapest way of producing electricity is via water but due to failed economies, lack of water in dams, and poor management of rainwater, we are facing an extreme energy crisis. The thermal power electricity, produced by oil and gas is highly expensive. Nuclear power stations are another means of energy, but nuclear reactors are highly affluent to set up for developing countries. Consumption of electricity is far greater than the production of electricity. There is an indispensable necessity to adopt new conduct to overcome this energy crisis.

Solar cells are the primary devices to deal with energy crises. These are based on the principle of the photovoltaic effect, a phenomenon that directly converts incident light into electricity via a semiconductor device such as a p-n junction. An electric field is set up by combining the two types of semiconductors. In the region of the junction where the field is formed, the positive holes migrate to the negative n-side and negative electrons migrate to the positive p-side. Because of the field setup, the positively charged particles move in one direction and negatively charged particles in the other direction. Light is composed of minuscule packets of electromagnetic radiation or energy which are known as photons [1]. Whenever a suitable wavelength of light falls on the semiconducting materials, energy is transferred from the photon to an electron causing it to jump to a higher energy level known as the conduction band (CB), thus producing current.

Due to photovoltaic installations, 100GW (Giga-watts) of electricity was produced at the end of 2030. 85% are using crystalline silicon, mostly cadmium telluride/cadmium sulfide in being polycrystalline thin film solar cells. Thin film solar cells have short energy reproduction time although these cells are cheaper. They have some disadvantages, they may become crucial while working in the terawatt range. Mostly they are composed of rare elements e.g. tellurium (rare as gold), gallium, and indium [2].

A new arrival to the Photovoltaic field has extended the solar conversion efficiencies to 15%, these solar cells are based on perovskite-structured semiconductors like methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$). These perovskites have high energy charge carrier mobilities because electrons and holes can travel huge distances when current is to

be removed, as they don't give up their energy in the form of heat within the cell. The perovskite cells have great importance as they are set up by spin coating (low-temperature solution method). For the eventual manufacturing of these cells, the easiest way of deposition is important. The lowest temperature (below 100°C) solution refined films have smaller diffusion lengths, although larger diffusion lengths can explain the photocurrents obtained with materials and high quantum efficiencies.

Three considerations that will affect the performance of these perovskites solar cells are mainly:- first is energy conversion efficiency. This aspect is in good shape because, with an efficiency of 15.4%, it works for several years and is near the theoretical limit, which is surprising, second is cost, this consideration is more perplexing because it involves energy reproduction time and energy cost as well as the presence of raw material. The minimum energy requirements in cell fabrication are translated through the low-temperature solution methods [2]. There exist no rare elements involving gold that have cheaper contact material alternatives. While there are some other possible replacements like tin, it will not be a key issue even in commercial cells if Pb is required.

The third consideration is stability. The study shows around a 20% decrease in efficiency after 500 hours. In fact, it is highly encouraging, when we observe the newly made inorganic cell stability; we observe the cause of optimization is that they can be made commercially important over the years.

Perovskites material like methylammonium lead halides (MAPbI) and all inorganic Cs-Pb halides are simple to manufacture and cheap to produce. Perovskites solar cells have become commercially attractive with the potential of having very low production costs and higher efficiencies. Perovskites have become a swiftly advancing solar technology in the modern era. The recent work on perovskites has been influenced by the absorber material based on methylammonium lead halides [3].

Perovskite performance can be extended in the solar spectrum to respond to a variety of wavelengths by controlling the material composition. The absorbing power of perovskites can be improved by introducing modifications in their composition. Perovskites solar cells of certain compositions may convert visible and ultraviolet radiations into electrical energy. There is a possibility that two perovskites having different compositions are combined, and they produce a perovskite-only tandem. Perovskites-only tandem solar cells can be fabricated on adjustable substrates with high power-to-weight ratios, which could turn competitors in tragedy retort and in defense operational energy areas. Alternatives are also being explored to reduce, evaluate, and potentially eliminate toxicity, and alleviate environmental concerns.

2. Silicon Solar Cells (SSCs)

Our Earth's crust is made up of 27.7% silicon which is the 2nd most plentiful element in the crust after oxygen. Silicon is also known as silica. Pure silicon is the fundamental component of traditional solar cells. SSC technology is referred to as the 1st generation panel as it has gained ground already in the 1950s. Even more than 90% of the current solar cell technology is based on silica. Pure crystalline silicon is a semiconductor material thus; it is a poor conductor of electricity. To overcome this issue, other atoms are incorporated with silicon atoms in a solar cell to improve silicon's conducting ability. After the addition of other atoms, silicon becomes a pure conductor and captures sun energy properly which is converted into electrical energy.

When solar cells were utilized for energy production, they set a revolution of change in motion. Solar cell technology is a continuously changing and evolving field which changed the face of energy production. For natural warmth, in the very early days, sunrooms were built. In 1839, the photovoltaic cell was discovered by a physicist, Edmond Becquerel, when he was experimenting with a cell in a conducting solution and the cell was made of electrodes. Willoughby Smith, in 1873 suggested that selenium could also function as a photoconductor [4]. After three years, Richard Evans and William Grylls applied the photovoltaic principle which was discovered by Becquerel. After 50 years, the photovoltaic effect was discovered by an American, Charles Fritz, who introduced the 1st working selenium cell. However, in modern solar panels, we use silicon in cells. The 1st SSC was proclaimed in 1941 and had an energy efficiency of < 1%.

In 1980, Si-based solar cells were prepared from crystalline silicon wafers. The evolution of work on the ultra-thin silicon substrate was energized by the very expensive cost of raw material polysilicon. In 2008, the price of silicon wafers was considered more than photovoltaic modules at 30% which was about 60% of the price of wafers obtained from wafering and bloom growth. In fact, a major selection of energies was used to fabricate photovoltaic modules to increase the energy reproduction time by silicon wafer manufacturing. So, prices of silicon were reduced in 2008 from about 400 to 30\$/kg with the continuous production of silicon solar cells in Korea and China in 2013. Thus, introducing an advanced wafer technology and expanding it into the present process chain remains an enormous challenge. Silicon solar panels are quite rigid and fragile which are not ideal properties for transportation. The fragments of silicon solar panels are much more expensive as compared to alternative options in solar technology techniques. Solar cells are made up of a material that is not abundant in nature and these elements are a necessity in this system. Silicon solar cells are very expensive. Silicon solar cells have less efficiency as compared to perovskites solar cells.

3. Perovskites-Based Solar Cells (PSCs)

Perovskites are a family of materials named minerals that have specific crystal structures. These materials are used to make solar cells having high-performance potential at lower costs. Due to their high efficiency, they have shown remarkable progress in this modern era. In a short time, they have become highly efficient. The majority of the recent work on perovskites is based on absorber material based on methylammonium lead halide. Perovskites except III-V technologies have exceeded all thin film technologies in power conversion. By tuning the material composition, perovskites can be used to respond to different wavelengths. Perovskites solar cells can be used to convert visible and ultraviolet light into electricity very efficiently and thus are the best hybrid tandem contenders for absorbers like crystalline silicon that alter infrared light efficiently. Two different compositions of solar cells can be joined together to constitute a perovskite-only tandem [5]. These tandem photovoltaics (PV) may lead to applications having higher efficiency and cost-effectiveness. These PSCs are competitive in disaster response, in mobile and defense operational energy areas, and can also produce on flexible substrates with power-to-weight ratios.

Among different methods used to fabricate perovskite solar cells, two major methods are:

- (i) Sheet to sheet: In this type, device layers are deposited on a rigid substrate; in the complete solar surface, they act as a front surface. It is commonly used in cadmium telluride modules.
- (ii) Roll to roll: In this type, the layers are deposited on a flexible substrate. In the complete module, they can be used as an exterior as well as interior surface.

Researchers have tried to use this type of device but they failed for significant commercial traction. But they are used in chemical and photographic film and paper products like newspapers. Various device structures and fabrications are available for further progress and perovskites solar cells.

In 1839, calcium titanium oxide ($CaTiO_3$) also known as calcium titanate was first discovered by German mineralogist Gustav Rose. At the end of the 18th century, work began on solar cells. It was discovered that selenium can generate electricity when interacting with light. It was seen that selenium-based solar cells were not able to store electrical energy through a device considering sunlight as a source. Charles Fritts explained the solar cell firstly which was made up of selenium wafer in 1883. The selenium solar cells were gold coated and fabricated with a conversion efficiency between 1 and 2%. The first photovoltaic cell constructed on silicon was invented by Bell laboratories in 1954. Gerald Pearson, Calvin Fuller, and Daryl Chapin explained that fabricated silicon photovoltaic cells can store power as electrical energy through sunlight. This energy was

sufficient to run an electrical instrument. This silicon solar cell had a modified 11% efficiency rather than 4%. In 1958, the Si-solar cell was considered in satellites for space purposes as an energy source. After the application of PV in satellites, it was used in off-grid power stations. In the 1970s, Elliot Berman prepared an economic PV. This application in grid stations was highly expensive. These PSCs have applications in domestic as well as railroad crossing. After that, the researchers started to work on thin-film solar cells. In 1980, the 1st thin film solar cell was fabricated at the University of Delaware by using cadmium sulfide and copper sulfide, the efficiency of which was more than 10%. In 2009, the hybrid organic-inorganic lead perovskite was first utilized for PV solar cells with visible light, having an efficiency of 3.8%. The first perovskite based on a stable solid-state was proclaimed with an efficiency of 9.7% in 2015, the research on perovskite solar cells gained momentum and their efficiency reached 21.5%, in the PV industry perovskites are considered remarkable candidates within a short time [5]. Perovskites solar cells have a greater tendency to absorb at higher wavelengths. PCE (power conversion efficiency) of perovskites is high compared to traditional solar cells and reaches up to 25.5% efficiency.

PSCs are mainly composed of PV absorbers, counter electrodes, and transport layers. In perovskites solar cells, the efficiency is determined by energy loss within the bulk. The manufacturing of PSCs absorbers doesn't need complex equipment. These absorbers as compared to silicon can be transferred at a lower temperature. They are not highly expensive as compared to silicon-based solar cells, where Si wafers are essential components of solar cells which make up 70% of the instrument. In DSSC (dye-sensitized solar cells), the PSCs were integrated first. The conventional dyes were replaced by using these solar cells. As compared to ruthenium, the PSSC (perovskites-sensitized solar cells) have a greater ability to produce electrical energy through photons. Unluckily such types of cells have less stability which can be affected by electrodes having liquids. The Redox couple has a corrosive nature and the device can be affected by this nature. However, there are some conditions where solvents can be leaked and an evaporation phenomenon can occur which inhibits the efficiency of this technology [6].

3.1 Structure of PSCs

Organic-inorganic perovskites have astonishing electrical, optical, and magnetic properties, better processability, and tunability of structure which has made researchers curious [7]. Due to these properties and some catalytic impacts, PSCs have great prospects in lasers, fuel cells, and the LED market [1]. The structure of perovskites has a resemblance with ABX_3 . In the center, there is a positively charged molecular or atomic cation (having positive charge) of type A. Perovskite cube also has B as cations of atoms at the corner,

and the faces of the cube have X as anions of smaller atoms having negative charge as depicted in Fig. 1.

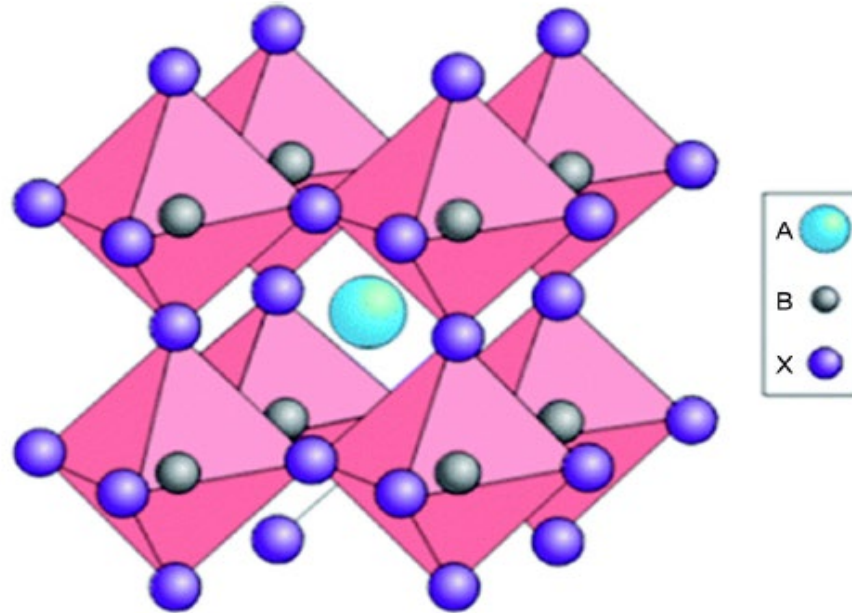


Figure 1. Cubic Crystal structure of Perovskite [1]

The excellent properties like superconductivity, and spintronics of perovskites are achievable if we know what types of atoms or molecules are used in perovskite. In the usual form of ABX_3 , the following composition of materials is used in organic-inorganic perovskites.

- A is an organic positive atom/molecule (cation) which is usually methylammonium or cesium.
- B is an inorganic cation that is often lead (Pb^{2+}).
- X is a small halogen (anion) often chlorine and iodine.

A little change in the organic component will affect the inorganic part of the cube because both are interdependent. The Group IV (lead) based PSCs have been most efficient because of good absorption in the visible region and their bandgap is also tunable. There are different reasons that Perovskite materials are preferred over other semiconductors because they have long carrier duration and mobility of modest nature even at low temperatures.

3.2 Optoelectronic Properties Of PSCs

As discussed in the previous section, PSCs have some unique properties that make them so important. Due to the optical absorption, perovskite just requires 500 nm thickness to have significant absorption in the visible region, whereas if we compare it to other solar cells [8], they need to have at least 12 μ m thickness to absorb significant light to produce charge carriers. The devices which are based on MAPbI₃ can have absorption over the whole spectrum till the red region ends, nearly 800 nm which is extendable to 1000 nm by using a Sn-halide combination in devices. Due to this property, perovskites are an important candidate for making tandem devices.

For MAPbI₃ the carrier diffusion length for both holes and electrons is almost 100 nm and for MAPbI_{3-x}Cl_x this goes to 1 μ m, as revealed by PL measurements. For MAPbI₃ devices there is a need for the mesoporous electron transporting material (ETM) because holes are more effectively extracted than electrons according to the reports. On the other hand, in Map(I₃)_{2x}Cl_x based devices there is no need for mesoporous ETM because the carrier diffusion length of holes and electrons already exceeds 1 μ m.

Instant charge generation is exhibited by MAPbI₃, because it is dissociated into high mobility charge carriers of about 25 within 2ps cm²/Vs. In about 1ps the electron is released into ETL (electron transport layer) of mesoporous TiO₂. But unfortunately, due to the intrinsic nature of TiO₂, it hinders the mobility of electrons that shall result in unbalanced charge transportation.

To have the complete information about band gap variation, Umari et al. did a complete analysis on density of states. There were some other peaks for MASnI₃ that extended from the point of main peak of band gap that were because of 1-p states. These peaks are not present in MAPbI₃. There is a rapid increase in levels of valence band (VB) in MAPbI₃ if contrasted with MASnI₃. In theoretical as well as experimental analysis of the band structure of electrons, spin-orbital coupling is an instrumental factor to be considered. The VB shift in MAPbI₃ is about 0.5eV greater than the CB shift which is simply the reason that the band gap of MAPbI₃ is superior to MASnI₃.

There are some essential optical properties that perovskites possess naming photoluminescence, electroluminescence, and non-linear optical effect [3]. When we use different halides like chlorine and bromine, they also show different optical absorption plus photoluminescence. With adding different metal ions at peak luminescence, the red shift is observed in PSCs.

The electronic properties depend on the inorganic part of the perovskite that further interacts with the organic part due to which orbital overlap changes, which is used for transporting carriers that will affect conductivity. The growth of double and triple layers

on perovskite also disturbs electrical conductivity. In 0D, the inorganic part is missing so its conductivity is seemingly lower than 1D and 2D perovskites.

3.3 Influence of A, B, and X site

3.3.1 A-Site

The A-site cation directly impacts properties like the electronic properties due to distortion of B-X bonding which is present in BX_6 octahedra, which arises due to the size effect [9]. The dimensionality for small cations like Cs and MA is 3. When radii keep increasing, the tolerance factor becomes 1, which results in packing symmetry of high order and a reduction in the bandgap.

Methyl ammonium (MA) cation is an extensively utilized cation in different perovskite optoelectronic devices. Due to a small bandgap and high symmetry, larger cations are also useful because they prove to harvest light at enhanced levels. Replacement of MA with different cations has also been tried with other larger cations like Cs but that hasn't worked because large cations alter the dimensionality from 3D to 2D resulting in large bandgap formation.

$MAXFA_{1-x}PbI_3$ perovskite material containing mixed cations which were introduced by Pellet et al. By optimizing the value of x in these materials the required optical properties are achievable. 14.9% power conversion efficiency was achieved in the current case. Certain regions giving better photocurrent arising from good absorption are responsible for giving better results than MA.

3.3.2 B-Site

Regarding the B site, Pb^{+2} , and Sn^{+2} are the most widely used metal cations in organic-inorganic perovskites. Because of superior stability and performance, lead is better than Sn. The stability of different elements in the periodic table starts to reduce on moving from lead to germanium in the table because the inert pair impact is reduced. The counterargument here is that electronegativity starts to increase which results in lowering bandgap and improving conditions for optoelectronic devices. So the possible best option would be an element from lower group IV-A also keeping in view the compromise with the stability of the metal.

The best possible way is the use of $MASnX_3$, which gives the band gap of nearly 1.2eV, but if we use $MAPbX_3$ then it gives nearly 1.5eV, interestingly the first one changes its oxidation state from +2 to +4, because of instant degradation which is caused by exposure of volatile SnI_4 product. Higher symmetry is possessed by Sn-based products, Pb based materials shall have lower symmetry. Tin-based materials have a better possibility of

generating photocurrent but rapid use in industry is hindered because of the stability issue that has been discussed earlier.

3.3.3 X-Site

Energy reduction occurs because of a redshift in the absorption of energy which is caused when we move in group VII and the atomic sizes of different halides start to increase. The electronegativity of halides starts to decrease when the atomic size is increased which resembles Pb at some point and gives increased covalent character. The most tunable part of perovskite is the halide part.

Iodine (I): The iodine-based perovskite has high efficiency of about 15% which makes it the most efficient and well-studied material. Pb and iodine together give a stable system because the covalent part of iodine matches well with Pb. Under some perturbation, this becomes oxidized, so this is one of the drawbacks that are noticeable and raises questions about stability issues. Due to this drawback, other options for substitutions of iodine have been examined.

Chlorine (Cl): the most important halide used in perovskite is Cl. Even with so much innovation and enhancement in devices, Cl application in optoelectronic devices is still studied rigorously [10]. The increased carrier life and high diffusion length are possible only due to the high efficiency of Cl-based perovskite materials. Miscibility of iodine with chlorine is higher than with Br due to enhanced efficiency. Cl having a high difference in radii and increased covalent character are the main reasons behind miscibility. It is also seen that mixed halide-based perovskite materials have highly oriented structures while on other hand, while chloride-based materials show simple cubic structures.

Fluoride (F): The property of being highly electronegative and being able to make hydrogen bonding with the other halides could make fluorine a good substitute [11]. But it also has drawbacks of having a big tolerance factor and increased lattice strain that prevents conductivity. The insertion of F in the form of $(BF_4)^-$ that modifies the formula like $MAPbI_{3-x}(BF_4)_x$, could make good hydrogen bonds with MA ions that shall decrease the chance of MA ions volatilization. Because of this inclusion, the conductivity is also lowered. This shows a band gap of about 1.5eV and a tetragonal structure.

4. Mixed Concentration of Perovskite Absorbing Layer

Hybrid organic-inorganic perovskites are very useful in science and technology, because of their tunable optoelectronic properties. The materials can be best described by the general structure like ABX_3 and here B and A are cations and X represents anions.

The highest symmetry is possessed by the ideal perovskite materials, i.e. cubic symmetry. In an ideal case, a Pm3m space group has the highest symmetry in cubic phase perovskite. A ABX_3 has a three-dimensional structure (3D) which is why it is a highly efficient perovskite. Usually, a halide anion motif $X_3 = (I^-, Br^-, Cl^-)$, monovalent cations ($MA, CH_3NH_3, FA, CH(NH_2)_2^+$) and divalent metal cations $B = (Pb^{2+}, Sn^{2+})$ are mixed [2].

4.1 A-site

The bond gap E_g is affected by changing the bond length and it is influenced by increasing *i.e.* ($FA^+ = 0.19 - 0.22nm$) or decreasing *i.e.* ($S^+ = 0.167nm, Rb^+ = 0.152nm$) the size of A. The shape of the perovskite grain is not affected by the concentration of Rb-mixing. But, perovskite film quality deteriorates and after mixing slightly, a blue shift occurs in photoluminescence (PL) peaks [12].

In history, for the first time, an A-mixed cation describing the band gap tunability of $MA_xFA_{1-x}PbI_3$ the based solar cell was proclaimed by Pallel et al. by changing the ratio of MA/FA. In Premixed $MA_xFA_{1-x}I$, the solution was isopropanol which was dipped in pre-deposited PbI_2 , so that MA/FA mixed perovskite can be synthesized and that the composition of $MA_{0.6}FA_{0.4}PbI_3$ produced the finest PCE of 13.4-14.52% with extending absorption edge up to 810 nm ($E_g \approx 1.53eV$) like Pure $FAPbI_3$. For the absorption range of the long spectrum enhancement, Lee et al. prepared $FAPbI_3/MAPbI_3$ films with assembled structure by ion exchange and reported the PCE of 16.01% and current density of $20.22 mAcm^{-2}$. The PCEs of 18.3% resulted in among the optimized MA^+/FA^+ with the composition of $(MA)_{0.6}(FA)_{0.4}PbI_3$ [1,13].

As we already know that inorganic material is more stable than organic material. Therefore, researchers started working on designs that work for inorganic monovalency in the perovskite structure. Choi et al. came up with $CS_x(MA)_{1-x}PbI_3$ PSC with $x = 0.1$ inverted composition: $PSS/CS_{0.1}(MA)_{0.9}PbI_3/P(BM)A/$ and attained power conversion efficiency of 7.86%. In an enhanced $CS_x(MA)_{1-x}PbI_3$ cell with $x = 0.9$, higher efficiency was attained reported by Niu et al. Moreover, $MAPbI_3$ has a higher thermal stability than an encapsulated device [12,13].

Rb^+ cations enhance both the performance of Rb-mixed perovskite solar cells and stability, although they have smaller ionic radii than Cs^+ ions ($0.181nm$). Park et al. examined (FA/Rb) PbI_3 and attained power conversion efficiency of 16.15% by using the same Rb quantity. Rb-mixed also got attention, because it enhanced stability against moisture at 85% RH [12].

4.4 Mixed B-Sites Cations

Large-scale application of Pb is restricted due to its toxic nature and therefore lead free alternatives were sought after. As in the periodic table, Sn and Pb belong to the same family. Therefore, Sn takes the place of Pb in the primary stage. The perovskite material is made with Sn^{2+} has a lower band gap than the perovskite material made of Pb^{2+} . Hence, to attain absorption near the infrared region we prepared perovskite material with mixed Sn and Pb [1,13].

It was found that it is possible to adjust the band gap within the range of $1.17\text{eV} - 1.55\text{eV}$. When Ogomi studied the optical properties of $MASn_{1-x}Pb_xI_3$ with varying ratios of Pb to Sn, the optical absorption wavelength was increased up to 1070 nm. A decrease in open-circuit voltage was noted due to the narrow band gap. In this whole process, lower power conversion efficiency was achieved because Sn^{2+} was easily oxidized to Sn^{4+} . In Sn-based perovskite solar cells, the conventional plane gave PCE of 5 – 6%. Zou et al. in an inverted planer heterojunction got PCE of 10.1% by synthesis of binary Pb-Sn perovskite ($MAPb_{1-x}Sn_xI_{1-y}Cl_y$) [13].

An impressive PCE of 13.9% was attained by Liu et al. with C_{60} -modified Sn-Pb perovskite film ($MAPb_{1-x}Sn_xI_3$). Hybrid Sn-Pb perovskite cell gives good performance and stability when disclosed in surroundings in the absence of encapsulation after perovskite solar cell modified with C_{60} . For improving stability, Marshall explained the addition of $SnCl_2$ in the light-absorbing layer, but it could not affect energy conversion efficiency [13].

4.5 X-Site

When we move down in the group of halogen atoms, the size of halides surges, creating the redshift of energy absorption. Mostly this occurs because the electronegativity decreases when the size of the atom increases and at indefinite time matches with Pb hence giving extra covalent character. The admirable studied material in the perovskite solar cell is iodide and iodide-based perovskite material gives efficiency as high as 16%. Iodide along with lead gives a very stable system because it matches nicely with Pb having a similarly covalent structure. But, the issue arises here because iodide is easily oxidized [1].

The most popular halide used in perovskite material is chlorine. As chlorine enhances diffusion length and carrier lifetime resulting in increased efficiency. Another fascinating effect of chlorine-doped halide perovskite is having fewer miscibility properties compared to bromine and iodine. We see this behavior because bromine and Iodine have smaller degrees of covalent character. It has been noted that $MAPbI_{3-x}Cl_x$ and $MAPbI_3$ with a maximum 3 - 4% Cl to I ratio has similar stoichiometry [1].

5. Requirements for Each Layer

5.1 Electron Transport Layer

PSCs are highly dependent on the type of material that is selected for the electron transport layer (ETL) in the context of efficiency and stability. The main property of ETL is that it should fulfill the band symmetry with the active layer. Transmittance of the ETL should be high so that photons can easily pass and can be absorbed by the active layer [14]. P-i-n and n-i-p are two types of devices based on the arrangement of the electron transport layer or hole transport layer (HTL). Due to the structure of ETL, n-i-p type PSC is classified into mesoporous or planar configuration. There are five types of layers present in both types of devices i.e., (i) TCO (transparent conducting device) such as (fluorine-doped tin oxide) FTO and (indium tin oxide) ITO (ii) electron transport layer (ETL) (iii) light absorbing layer (iv) hole transport material (HTM) (v) metal or non-metal electrode [15].

The presence of ETL is vital for the high performance of PSC, for maximum electron collection and for transferring electrons from the perovskite layer to the electrode. Some groups claimed that without using ETL, they achieved 14% PCEs but the ETL layer in PSCs was more effective in terms of stability and performance. Jurez-Perez *et al.* noted that the absence of ETL slightly affects V_{OC} (Open-Circuit Voltage) but strongly influences J_{SC} (short circuit current density) and critically reduces it. The absence of ETL also reduces the fill factor which has a direct influence on the power conversion efficiency of the devices. Electron-hole recombination increases in the presence of ETL at the small cost of an increase in series resistances. Power conversion efficiency decreases from 14.1 to 11.5% after the removal of ETL as observed by Zhang and co-workers. Ke *et al.* reported that power conversion efficiency was 14% but complete cells showed power conversion efficiency of 16% and there was no sign of stabilized power observed in the absence of ETL, however, PCE achieved from this current-voltage measurement was a little high [15].

To manufacture high-efficiency perovskite solar cells, the nominated ETL material must satisfy several criteria such as (i) Electrons must move fast within ETL so electron mobility of material must be decent (ii) To ensure high transparency, the band gap of incident light passing through material should be wide (iii) Compatible energy level. Further in ETL planar heterojunction, the semiconductor material selected must have (i) a good anti-reflection to lessen the transmittance (ii) a compact structure to prevent direct contact between transparent conducting oxidize and perovskite. Generally, two ways are used to improve the properties of electron transport layers (i) modifying the structure of ETL and (ii) using a material with better optoelectronic properties [15].

5.1.1 Different ETL Material Used In Perovskite Cells

TiO_2 , ZnO , SnO_2 and ZrO_2 are some metal oxides that are commonly used as ETL. Each of these materials has its own benefits to enhance power conversion efficiency. Two types of processes are introduced to fabricate perovskite solar cells. One is based on one step-deposition, which gives a PCE of 7.23% in comparison to a TiO_2 based perovskite solar cell. To control shunt resistance, we need optimum porosity over the layer of perovskite [14].

Yella et al. modified the particle size of rutile TiO_2 successfully by using chemical bath-deposited rutile thin film to give PCE as high as 13.7%. Luo et al. explained the complete list of hole injection, electron injection, and exaction annihilation. It is very difficult to define the characteristics of an ideal ETL due to the large variety of ETL/ETM. Using SiO_2 , Al_2O_3 and ZrO_2 (as scaffold material), high efficiency was reported. A research group reported that they achieved $\sim 10\%$ PCEs by using SiO_2 , Al_2O_3 and ZrO_2 . We can successfully form a perovskite layer, block holes and inject electrons, when the CB edge (CBE) is lower and the VB edge (VBE) is higher, which can improve the recombination resistance. Smooth electron injection is observed in both SiO_2 and ZrO_2 , because for SiO_2 and ZrO_2 , the much higher CBE and band gap is large, as a result electrons stay in the CB of the perovskite layer for a much longer time [14].

Bi et al. described that ZrO_2 had a higher efficiency than TiO_2 after a comparison of both the scaffold materials was drawn. ZrO_2 had PCE = 10.8% and TiO_2 had PCEs = 9.8%. ZrO_2 is an efficient scaffold material because of higher photo-voltage and electron lifetimes, although the band alignment was not fulfilled [14]. It has been reported in the literature that using organic semiconductors, metal oxide-free perovskite solar cells have been achieved. In order to get lofty efficiency in inverted PSC organic ETL such as [6, 6]-phenyl C61-butyric acid methyl ester (PCBM), poly (3-hexylthiophene) (PEHT), PEHT: PCBM composites. PSC can be made with enhanced performance and efficiency by using organic material with a metal oxide scaffold blocking layer. The LUMO of such materials should be lower than that of the active layer, this condition is also satisfied by many organic materials. An ETL was made by NiO_2 , scaffold blocking layer and HTL was made with $PCBM/BCP$ as reported by Wang et al. Furthermore, 16.21% efficiency was attained with an extraordinarily high $V_{oc} = 1.05V$ and $FF = 0.78$ with planar heterojunction device constructed as $ITO/PEDOT:PSS/Perovskite/PC_{61}BM/Cu/Al$ reported by Chiang et al. [14].

5.2 Hole Transporting Layer

The hole transport layer is basically used for three purposes. First, to avoid the straight exposure of metal electrode with mesoporous TiO_2 perovskite, it is placed prior to the gold

electrode, as a result, V_{oc} is increased and greater luminescence performance is achieved because recombination is reduced. Secondly, by decreasing the (diffusion) losses of charges in HTL, the illumination wavelength is increased and the central quantum efficiency is independent of applied voltage. Third, allowing an alternate way for light to pass between the absorber layer, the reflectivity of the gold electrode is increased due to hole transporting layer. These effects enhance short circuit current density [16].

5.2.1 Hole Transporting Material (HTM)

Polymeric, inorganic, and small organic HTMs are basic categories in which solid-state hole transporting materials are divided. Inorganic materials have high hole mobility, low cost, and good properties, hence these are used in PSCs, such as NiO, CuI, and CuSCN. But the stability of devices based on these materials is affected. Complex purification processes, poor infiltration into nanostructured material, low solubility, and tricky characterization are some drawbacks of polymeric materials [17].

5.2.2 Inorganic P-type semiconductors as HTMs

HTL inorganic materials were investigated due to their large hole mobility, low-cost construction, and intrinsically high stability. However, there is a small drawback as in mesoscopic PSCs, the solvent utilized for deposition dissolves within the perovskite. Kamat and co-worker attained a PCE of 6% for copper iodide (CuI). Due to low V_{oc} , poor PCE was achieved, while the highest value of fill factor (F) (0.77) was attained, which can be credited to high recombination measured by impedance spectroscopy. Copper thiocyanate (CuSCN) being transparent to the infrared and visible region, and possessing high mobility was used as HTM initially by Ito et al. into a mesoscopic PSC. CuSCN under standard AM1.5G irradiation gives a maximum PCE of 86% when deposited by a doctor-blade process. PCEs of 12.4% was recorded after optimization of the thickness of the hole transport material (600-700nm). Because of effective charge removal from perovskite and by using CuSCN in a planar structure perovskite solar cell, a high J_{sc} (19.7mAcm^{-2}) was achieved. Bian and Liu et al. achieved an impressive PCE of 16.6%. HTM up to 57nm of thickness by electrode position and MAPBI_3 formation was used in a one-step fast deposition crystallization method. In DSSC and OPV, nickel oxide was utilized as hole transporting material, and a power conversion efficiency of 7.26% was achieved by Sarkar et al. by using a layer of NiO placed by electrode position in an inverter planar structure [17].

5.2.3 Organometallic HTMs

In mesoscopic PSCs, CuMePc (tetramethyl- substituted Cu” phthalocyanine) was utilized as a hole transporting material and it enhances the efficiency in comparison to unsubstituted phthalocyanine. The reported PCE was only 5%; although it was hypothesized that methyl substitution would increase the $\pi - \pi$ interaction. The molecular construction of hole transporting material commonly contains some electron-rich groups conjugated to the inner aromatic core cell called HTM core. Triazines, thiophenes, diketopyrrolopyrrole, triarylamine and spiro-liked HTMs are some examples of conjugates that have been reported. By changing *P - OMe* with several alkyloxy groups, many Spiro-OMeTAD analogues were constructed. Spiro-OMeTAD is of a high-glass transition temperature T_G and has exact energy level and in PSCs, it is still more effective as several hole transporting materials. Hole-mobility, μ_b of pristine Spiro-OMeTAD was decided by (SCLC) space charge limited current and it was about $2 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ [17].

5.3 Absorbing Layer

In a perovskite solar cell, an absorber layer is a perovskite layer that provides free electrons and holes after absorbing light. Upon the action of an electric field, these free charges diffuse and drift away. In short, electrons move towards HTL and holes move toward the ETL. The ability of transporting holes and electrons toward their respective layers gives the efficiency of the absorbing layer. The electron dissipates energy, when holes and electrons are collected by their specific electrode, and before returning to the device at the opposite side, electron, and hole recombination occurs. It will recombine with the hole if electrons are not extracted by the electron transport layer. This is nothing but a radiative transition, in which a photon of energy equal to the band gap is emitted.

5.3.1 Preparation Method of The Perovskite Light Absorbing Layer

Roughly there are three main types of synthesis processes commonly used for light-absorbing layers of perovskite solar cells such as the vapor-assisted solution method, vapor-deposition method, and the solution method. In the vapor-assisted solution method, the HTL directly touches the electron transport layer and produces a synthetic crystal, thus the open circuit voltage and filling factor are reduced. But, the solution method is easy and inexpensive. Using vapor deposition method, the perovskite film so formed has a high surface density and hence enhances the open circuit voltage as well as the filling factor. However, this process involves high energy consumption and a high vacuum is required. If we integrate the advantages of solution and evaporation methods it is known as the vapor-assisted solution method [18].

6. Fabrication Techniques

The quality of the absorber layer film affects mainly the performance of other layers of PSCs exhibiting equal performance. To find the quality of the film, surface morphology of the substrate being used is preferred for the fabrication from the several factors of high quality film. To get good device performance and high quality film, the substrate being used is usually mesoporous. The various deposition techniques for the construction of PSCs are 1-step deposition, 2-step deposition, vapor deposition method, spin coating, and TVP (thermal vapor deposition) [2].

6.1 One-Step Deposition

1-step deposition method has been mostly used by scientists as it is a reliable process and cheaper. Perovskite precursor and pinhole-free is the technique used in the fabrication of perovskite film. In a single-step deposition, the organic solvent is mixed with the following; “MX₂ (M is Pb or Sn and X is Br and Cl) mixture and formamidinium iodide (FAI) or methylammonium iodide (MAI)” as the perovskite precursor. This mixing of MAI or FAI (organic halide) and MX₂ (Inorganic halide) in an organic solvent, a pure phase, pinhole-free, and a dense perovskite is obtained by spin coating and tempering in the range of 100-150 °C [19]. A one-step deposition is preferred due to slow crystallization in the fabrication process. Another factor One-step deposition gives us is that these are some conditions that determine the quality of perovskite film. The conditions are tempering, humidity, the substrate being used, and as well as film thickness. The two parameters that are important for a good-quality film are film thickness and morphology [20].

6.2 Two-Step Deposition

In order to expose organic ions in perovskite film, whether the ions are in solution or in vapors, PbI₂ is spin-coated on the substrate [21]. After this spin coating of lead iodide (PbI₂), there is a dipping of the substrate into an isopropanol solution of methyl aluminum iodide (MAI). For the formation of perovskite having organic and inorganic metal halide, PbI₂ is again spin-coated onto the MAI. This method is being used for the uniform and controlled fabrication of thin film in the PSCs [1]. With a certified PCE of 14.14%, two-step deposition first showed 15% of PCE. In this method, PbI₂ is not completely converted, and also crystal size is not controlled with surface morphology. So different post-operative methods have been revealed [21].

In one-step deposition, a comparatively smaller film thickness of 250 nm is obtained while it is found that two-step deposition leads to a film thickness of approximately 280 nm. Field emission scanning electron microscope (FESEM) gives the surface morphology of the film as illustrated in fig. 2. While distinct perovskite grains are obtained by heating the precursor

This is a free preview.

For the entire book please visit us at

<https://www.mrforum.com>

Please also consider supporting us by letting your library know about MRF. Maybe they will be able to start featuring some of our books in your library.

Thank you for your help and time.