

PEROVSKITES- A COMPLETE OVERVIEW

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Abstract— Currently more than 85% of the world's energy demands are met by combustion of fossil fuels which has numerous deteriorating effects on the environment (CO_2 emissions). Industrialization has resulted in an additional 15-terawatt energy demand on a global level by 2050. Solar cells using semiconductors have high Power conversion efficiency (PCE) > 20%, but their high production and maintenance cost becomes an obstacle for a large-scale implementation of silicon or other semiconductor based solar cells.

A sizeable portion of the cost of solar cells comes by using photoactive materials which consume a lot of energy, hence increasing the costs. The inorganic components can be replaced by semiconducting polymers, which have been found to be more cost effective, with higher conversion efficiencies.

The advent of perovskites has revolutionized the photovoltaic technology, to a very large extent. They have been shaping up the progress of third Generation photovoltaic cells for quite some time.

They are very simple in structure, but they have the capabilities for highly cost effective and eye-opening discoveries, which may prove to be a blessing for the advancement of photovoltaic technology, which still is an evolving field.

The average power conversion efficiency (PCE) that photovoltaic cells could deliver was 5%. But ever since perovskites have come into use, the power conversion efficiency has been boosted up to greater than 18% up to almost 22% in a matter of just six years, thereby rivalling the third-generation thin film silicon PV cells.

Index words – Perovskites, Power conversion efficiency (PCE), Photovoltaic cells (PV cells)

I. INTRODUCTION

Perovskites are materials which have a general formula ABX_3 , where X is an anion, A and B are cations which have different sizes from one another, "A" having a larger size than "B" [1]. In this review paper we have given an overview of perovskites, also analyzing the compositional engineering to maximize the yield of perovskites while keeping in mind the temperature and component dependent degrading experienced by perovskite materials.

PV cells that can be employed as a thin film have been under development for quite some time now. Thin film technologies which used materials such as Cadmium Telluride (CdTe) and Copper Indium Gallium Selenide have PCE as 19.65% for 1cm^2 area. But large-scale production could not be achieved [2].

Dye sensitized solar cells (DSSC) are one of the most developed PV technologies. Nanostructured TiO_2 acts as an electron conductor and a dye (perovskite) absorbs the

sunlight, which is continuously regenerated and a counter electrode to collect electrons is employed. Lab tests showed PCE for DSSC > 13% and the actual module gave PCE close to 10%. [3,4].

But the use of liquid electrolyte in DSSC raised questions about its stability and commercial viability. Hence solid-state dye sensitized solar cells (ss-DSSC) came into the picture. They use solids for dye regeneration and hole transfer.

When the compositional engineering aspects were studied and after investigating many factors like phase stability, morphology of the perovskite layer, hysteresis which was observed while observing current-voltage characteristics, and overall performance as a function of chemical composition a conclusion was drawn that incorporation of methylammonium lead bromide ($MAPbBr_3$) into formamidinium lead iodide ($FAPbI_3$) stabilizes the perovskite phase in $FAPbI_3$ and the power conversion efficiency of solar cell is improved by more than 18% when it is exposed to a standard illumination of 100 milliwatts per square centimeter. "A" should fit into the space of 4 adjacent corner sharing MX_6 octahedra to form a closely packed perovskite structure [6].

Perovskites are ideal photovoltaic materials due to their many qualities like high solar absorption, ease of fabrication and low non-radiative carrier recombination rates. Although we have to take into consideration the fact that most of Perovskites have Lead (Pb) as a major constituent which raises toxicity issues during fabricating and disposal of the device. Also, they generally undergo degradation on exposure to moisture and ultraviolet radiation [1].

The most recent developments have engineered Perovskites whose PCE exceeds 20% [NREL efficiency chart]. Methylammonium lead halide perovskites ($MAPbX_3$) is the most promising class of perovskite materials for PV applications with the additional advantage of altering the properties exhibited by these materials by varying the type of halide ions [7].

Perovskites are sensitive to heat, moisture, increased light intensity and other factors. Measuring the efficiency and stability of a perovskite is a must in order to analyze the material completely. Although measuring efficiency is a matter of minutes even seconds, but stability assessment could take several a very long time (several months or even a year). Introduction of increased stress factors can accelerate the degradation rate as compared to the degradation under standard operational conditions [8]. It has been demonstrated that concentrated sunlight can be used for organic PV accelerated degradation testing [9,10].

II. UNDERSTANDING PEROVSKITES AT A BASIC LEVEL

A simple AMX_3 type of arrangement can help in understanding the basic structure of perovskites where M is a metal cation and X is an oxide or halide anion. Perovskites form a MX_6 octahedral arrangement, where M is the center of an octahedron with X at the corners.

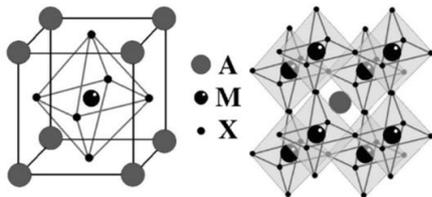


Figure 1: Left: Ball and stick model of basic perovskite structure. Right: Extended perovskite network structure connected through corner-shared octahedra.

A can be Ca, K, Sn, Pb. The basic requirement for a closed-packed perovskite structure is that the cation (A) must fit in the hole formed between the eight corners of the octahedron. The size of the cation and the anion regulates the electronic and optical properties of the perovskite material. In ideal conditions, perovskites should have a cubic geometry, but they are pseudo-cubic or distorted in nature [5].

Two dimensional perovskites structures can be formed as well. A suitable cationic organic molecule can be used as “A”. This is referred to as the organic part. The inorganic part consists of the MX_6 octahedra. The inorganic part is trapped between the organic molecules which have cationic properties which leads to an alternating placement of the organic and the inorganic part which leads to the formation of two-dimensional organic inorganic layered perovskite [11].

Perovskites having a general form of $CH_3NH_3MX_3$ were

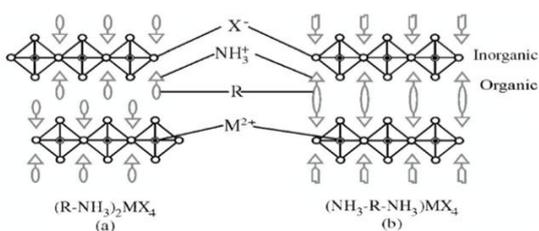


Figure 2: Structures of 2D organic-inorganic perovskites with a) a bilayer and b) a single layer of organic molecules.

employed as active layer for field effect transistors [12] and electroluminescent devices [13, 14]. The direct band gap of perovskites (which is fairly wide) can be regulated by varying the alkyl group as well as the metal ion. We can thus

conclude that the size, structure, conformation, charge of the organic cation determines the properties of the perovskite materials [15, 16].

III. EMPLOYMENT OF PEROVSKITES TO MANUFACTURE PHOTOVOLTAIC DEVICES

Perovskites are found to have unique optical properties [17], excitation properties and high electrical conductivity [19]. Perovskite compounds of the type $CH_3NH_3MX_3$, which possess different energy gaps [17], can be used to optimize the performance of the photovoltaic cell. The energy gaps can be adjusted by changing the alkyl group, halogen atom or metal atom. Organic-inorganic perovskite compounds such as $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$ are extensively used as visible-light sensitizers in photovoltaic cells.

$CH_3NH_3PbX_3$ (X=Br, I) perovskite nanocrystals as sensitizers (light harvesting layer) in liquid electrolyte-based DSSCs were tested. Lead Bromide ($CH_3NH_3PbBr_3$) based cells gave a photo-voltage of 0.96 V [1]. Incorporation of Iodide redox shuttle improved the PCE at 1 sun illumination (1 sun=100 mW/cm²) to 6.54% [20]. But the performance of such devices depleted due to dissolving of perovskites in presence of liquid electrolyte. To avoid this, an insulating layer of aluminium oxide was inserted between the perovskite sensitized TiO₂ layer and the liquid electrolyte. But it did not lead to any significant improvements.

To counter the problems faced in liquid electrolyte-based devices solid mesoscopic cells began employing perovskite as sensitizers. The perovskite compounds of the form $CH_3NH_3PbX_3$ (organometallic halide) and $CH_3NH_3PbI_2X$ (mixed halide), which serve as the key materials for making high efficiency solar cells, use TiO₂ as the electron-transporting medium. A thin film mesoporous TiO₂ is deposited on top of a blocking layer on a glass substrate which is made up of transparent conducting oxide (TCO). The blocking layer is a compact layer and prevents direct (electrical) contact between the hole transporting material (HTM) and the TCO. To achieve high performance, it is necessary to ensure that the HTM penetrates into the pores of the mesoporous film of TiO₂. A thin photo anode layer is thus necessary to facilitate the filling of pores. The penetration of HTM into the pores of Nano particulate TiO₂ films is due to its complicated mesoporous structure. This has led to the unfolding of better structure of TiO₂ such as nanotubes or Nano rods, which may enable the HTM penetration. But the efficiency was low in this case resulting in reduced light harvesting abilities. One of the ways to improve the efficiency of the Nano rod based solar cell is to increase the coverage surface area. Alternatively, we can choose a sensitizer with high extinction coefficient. For a good photovoltaic performance, the HTMs need to satisfy a given set of conditions. These include thermal stability, UV stability and sufficient hole mobility. Also, the HOMO (Highest Occupied Molecular Orbital) energy levels must be well-matched [22].

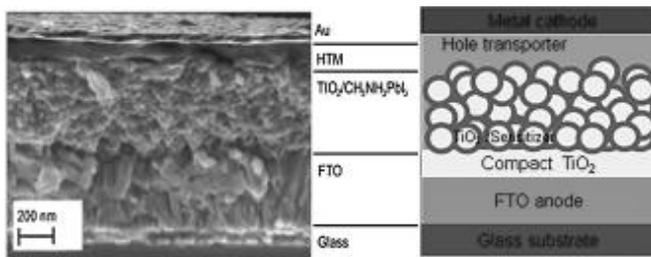


Figure 3: The left image shows cross-sectional view of perovskite-sensitized solid-state mesoscopic solar cell. On the right is the schematic diagram of solid-state mesoscopic solar

Lee et al. [23] discovered that the perovskite compound $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$ suffices both as an electronic conductor and a light harvester in meso super-structured solid-state solar cells (MSSCs). These MSSCs are a new generation of hybrid solid-state photovoltaic devices since they do not use a photo anode of mesoporous TiO_2 . These devices reported a notably high photovoltaic conversion efficiency of about 10.9%. A high photocurrent ($17.8\text{mA}/\text{cm}^2$) is the main reason behind the high efficiency of MSSCs. This high photocurrent is a result of extended perovskite absorption to ca. 800 nm and the high photo voltage of 1 V, arising from the crystalline structure of the electron conductor [22].

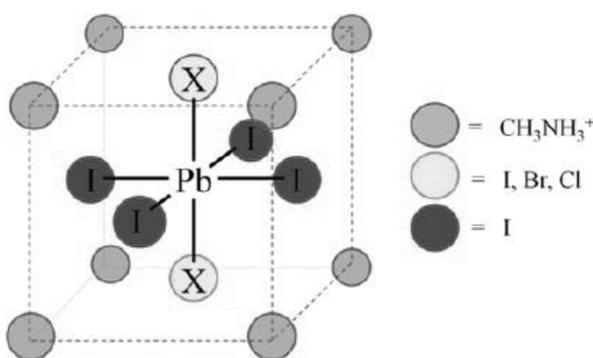


Figure 4: An illustration of the structure of the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_2\text{X}$ ($\text{X}=\text{Cl}, \text{Br}$ or I). I atoms occupy the equatorial positions while X atoms occupy apical positions.

IV. UNDERSTANDING THE ELECTRONIC PROPERTIES OF PEROVSKITES

DFT (Density Functional Theory) calculations were made to improve the understanding of electronic properties of mixed halide perovskites of the form $\text{CH}_3\text{NH}_3\text{PbI}_2\text{X}$. The values of the optical band gaps obtained after running the DFT calculations were fairly matching with the values that were procured experimentally. These calculations also detected the presence of two different types of structures with different electronic properties for mixed halide perovskites. When $\text{X}=\text{I}$, the 2 structures are found to have almost similar properties. But when $\text{X}=\text{Br}$ or Cl the properties exhibited by

these 2 structures differed. The formation energy is highest when $\text{X}=\text{I}$, followed by Br and then by Cl [5]. The H-bonding between the ammonia groups and the halides, account for the difference in structures and the efficiency with which light is converted to electricity.

V. PREPARATION OF PEROVSKITES

The most commonly synthesized organometallic halide perovskite is $\text{CH}_3\text{NH}_3\text{PbI}_3$, which is a lead halide perovskite. There are mainly two methods for the synthesis and deposition of perovskites.

- 1) Solution based methods
- 2) Vapor phase methods

In the methods, the lead halide is synthesized first followed, by the exposure to the methyl ammonium halide, which then yields the perovskite. The two methods are as follows -

A. Solution-based methods

This is the simplest method for deposition of perovskites. It involves the precipitation from the solution. The lead halide and the organic halide (methylammonium halide in this case) are dissolved in the solvent. Solvents most commonly used for this purpose are mainly Lewis bases such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) [24]. It involves solid state reactions at elevated temperatures. The perovskite crystals obtained are in their purest form, owing to the availability of impurity free precursors. Solvents like these, coordinate with the lead halide salts, and form lead halide complexes in aqueous solutions of halide. The structure of the resulting perovskite crystals depends mainly on the following factors [24]:

- Choice of solvent used
- Mode of removal of solvents
- Structure of the substrates

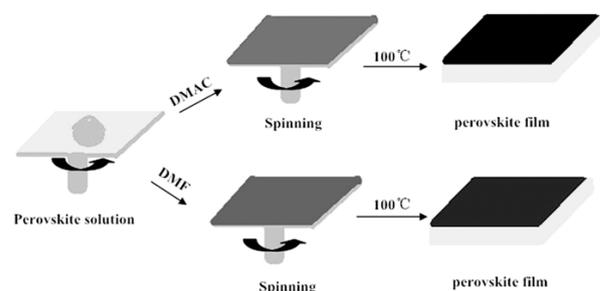


Figure 5: Solution based method for preparation of lead halide perovskites, using lewis bases such as dmf and dmac as solvents [2]

The single step solution process is the most preferred method for preparation of controllable mixtures of perovskites.

The perovskites created here have higher band gaps than the common $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite, such as $\text{I}-\text{Br}$ and $\text{Br}-\text{Cl}$ perovskites.

In this, the stoichiometry of the resulting crystals

deposited on the films is similar to that followed by the precursors in solution.

A two-step approach has been formulated, which in turn produces perovskites with higher efficiencies, as compared to the single step process.

In this approach, either lead chloride (PbCl_2) or lead iodide (PbI_2) is dissolved in DMF. The resulting solution is then deposited onto a substrate, and then dried into a film. The film is then either directly dipped into an alcoholic solution of excess $\text{CH}_3\text{NH}_3\text{I}$, or it undergoes continuous spin coating with such a solution, which converts the lead halide to the final perovskite crystals. This is a sequential deposition technique.

Production of mixed halide perovskites is also possible through this method. Films of mixed-cation mixed-halide perovskite can be prepared from a solution of MABr, FAI, PbBr_2 and PbI_2 in a solvent which is a mixture of Dimethyl Sulphoxide (DMSO) and Dimethyl Formamide (DMF). The molar ratio of $\text{PbI}_2/\text{PbBr}_2$ is fixed to 5.67 and that of PbI_2/FAI (RPbI_2/FAI) is fluctuated from 0.85 to 1.54. This method enables us to fabricate the PSC. The maximum value of PCE for this cell is 20.8% and it is achieved with RPbI_2/FAI as 1.05. The device has open circuit voltage (VOC) = 1.16 V, short-circuit current density (JSC) = 24.6 mAcm^{-2} and fill factor (FF) = 0.73 [43]. The biggest limitation of this approach is that despite producing perovskites of higher efficiencies, a lot of time is consumed in producing thick films, as well as higher temperatures are required.

B. Vapor-phase methods [24]

These methods are used to produce hybrid perovskites. The crystal structure and properties of the perovskites produced by these methods differ from that produced by solution-based methods. It involves Co-evaporation of Lead Chloride (PbCl_2) and $\text{CH}_3\text{NH}_3\text{I}$ in a vacuum deposition chamber. This results in uniform perovskite films, with remarkable PV characteristics.

The composition of the final perovskite product is largely dependent on the rates of evaporation of the precursors.

It is found that the resulting perovskite has a cubic structure, whereas at room temperature the perovskite shows tetragonal geometry.

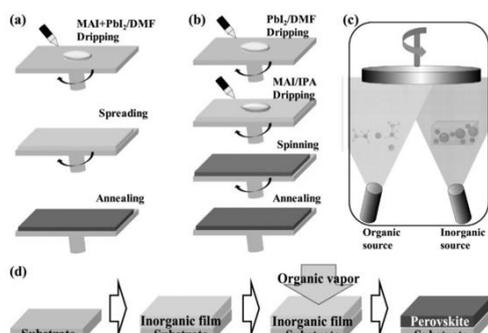


Figure 6: Four general methods for preparing perovskite active layers. (a) One-step precursor deposition. (b) two-step sequential deposition method, (c) DSVD and (d) VASP. [26]

Similar to the solution-based methods, even for Vapor based methods there is a two-way approach. In this approach, lead iodide (PbI_2) is deposited from the solution, and then converted to perovskite by the action of $\text{CH}_3\text{NH}_3\text{I}$ vapor.

By this two-way approach, we get pure forms of iodide, bromide and chloride perovskites, along with some mixtures.

The Chloride (Cl^-) ions have an important role to play in the deposition process, to improve the perovskite photovoltaic performance. They play a vital role in complex ion equilibrium and in the nucleation of the reaction. This results in peculiar structural diversity, which is seen in the product perovskite films.

Presence of chloride also improves the overall lifetime of the perovskite, and also enhances the diffusion length traversed.

VI. APPLICATIONS OF PEROVSKITES IN SUPERCONDUCTIVITY

A solid-state reaction has led to the synthesis of new layered pnictide oxide (Fe_2P_2) ($\text{Sr}_4\text{Sc}_2\text{O}_6$). The basis for this reaction was the remarkable discovery that LaFeAs had a high critical temperature. All the related phosphide oxide and chalcogenide materials and other superconducting materials which contain anti-fluorite iron pnictide layers have been discovered which has given an impetus to the field of superconductivity using perovskites.

The main advantage of materials with similar stacking structures of perovskite-type oxide layers is that due to the extreme flexibility in the perovskite-based structure, variety of transition metals in the perovskite block have been reported.

Pnictide having a perovskite oxide layer has been reported to have properties of a superconductor due to its chemical and physical variance.

The samples containing Sc-22426 as a main component were analyzed. It consisted of a stacking of antiferroite Fe_2P_2 layers and perovskite based $\text{Sr}_4\text{Sc}_2\text{O}_6$ layers [27].

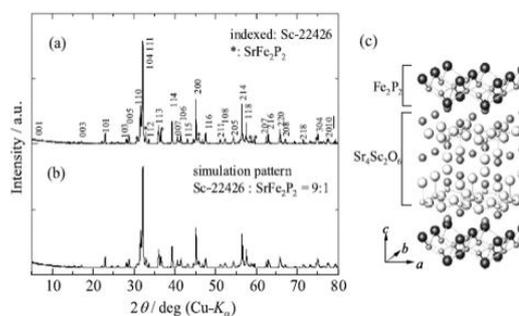


Figure 7: Power XRD pattern of Sc-2246 a) calculated XRD pattern of the mixture with Sc-2246: $\text{SrFe}_2\text{P}_2=9:1$ b) and crystal structure of Sc-22426 c) Stars indicate positions of diffraction peaks due to secondary phase, SrFe_2P_2

The study and analysis of these compounds and molecules depict that the perovskite layer in the pnictide oxides could be used as a superconductor and using these superconductors and its constituents could bring in a revolution and will give impetus in the effort to search for pnictide based

superconductors. The sample analysis of the newly synthesized iron pnictide oxide Sc-22426 gave the following results [27]:

It has the longest reported Fe-Fe distance amongst all other class of iron pnictide oxide compounds.

A superconducting transition of about 15-20K in the critical temperature was observed in the magnetization and resistivity measurements.

The tetrahedral symmetry in at the FeP layer was responsible for the high critical temperature of this oxide.

VII. EFFECT OF HUMIDITY ON PEROVSKITES

Humidity plays a very critical role in degradation of PSC performance. The overall reaction is given by [37]



In the reaction mechanism, CH_3NH_2^+ is de-protonated by H_2O . This increases the band gap. Degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ also results in the formation of compounds such as PbCO_3 and $\alpha\text{-PbO}$ [38]. It was found that $\text{CH}_3\text{NH}_3\text{PbI}_3$ undergoes complexation with H_2O giving monohydrate ($\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$) [39] and dehydrate ($(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$) [40]. Single perovskite crystals when exposed to moisture also undergo degradation. However, the rate of reaction will be much lower in this case. This is because in perovskite films, water molecules can penetrate easily due their abundant grain boundaries. But however, the hydration of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was found to be a reversible reaction [41, 42]. In other words, pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ can be recovered by moisture removal.

VIII. TEMPERATURE DEPENDENT DEGRADATION OF PEROVSKITES

The temperatures to which the material is exposed and the halide ions present in the perovskite determine the light harvesting properties at those particular conditions. The ratio of the photons absorbed by a film of perovskites exposed to degrading conditions (high temperature and concentrated sunlight) to that of a film which was not exposed to any of these conditions (as-produced) was measured. It was found that the ratio declines as the time of exposure to concentrated sunlight increases [29]. The cause for this effect may be the crystallization of PbI_2 from the perovskite material. Several mechanisms were put forth which tried to explain the above observations. These mechanisms suggested that MAPbI_3 decomposed to MAI and PbI_2 , with further breakdown of MAI to its constituents like methyl amine, water etc. [30, 31]. To check whether sunlight was a contributing factor, similar ratios as above were measure for a film which was heated to temperatures ranging from 25-75 degree Celsius in dark, but degradation of material was not observed [8].

Now a different set of experiments was conducted wherein the illumination was kept constant and the temperature was varied at the same illumination. Degradation in absorption, or decomposition was not observed at lower temperatures, and it increased with increasing temperature. This was proof

that the phenomenon of degradation is thermally accelerated [8].

Hence, exposure to light and heat combined, contributes to the degradation of perovskites and illumination is required to initiate degradation of absorption.

The proper confinement of perovskites or their encapsulation is of utmost importance to prevent degradation and in order to make this unique photovoltaic technology commercially viable and to facilitate its implementation on larger scales.

Now similar experiments were carried out with MAPbBr_3 perovskites. The samples were exposed to 100 suns (1 sun=100 mW/cm²) and the sample temperature was high (45-55 degree Celsius). The results obtained in this case were different than the ones obtained for MAPbI_3 . There was no degradation in absorption and the onset for all the spectra was in accordance to the optical band-gap of MAPbBr_3 (2.3 eV) [19].

This difference in the properties of MAPbI_3 and MAPbBr_3 is due to the difference in the bond strength of Pb-I and Pb-Br. The Pb-Br bond is found to be shorter and hence stronger than the Pb-I bond. Hence decomposition of MAPbBr_3 is harder as compared to that of MAPbI_3 [33].

But the enhanced stability of bromide perovskites is countered by its high optical band gap of 2.3 eV. This makes the use of bromide perovskites in single junction devices highly inefficient [34].

Using mixed halides perovskites ($\text{MAPbI}_{(3-x)}\text{Br}_x$) would be the solution for obtaining highly efficient PV devices which also guarantee the stability to ensure its industrial viability.

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