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**- THESIS-**

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**THEORETICAL STUDY ON PEROVSKITE SOLAR CELLS (Pscs) AND THEIR  
APPLICATIONS**

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Defended on: 11 /06/ 2022 before the examination board

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The courage, the will, the health and the patience to complete  
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the honor they have done us by accepting to evaluate our work.

## **Dedication**

First of all, I would like to thank the good

God who brought me to the end

my studies.

I dedicate this work:

To my parents, to my dear mother who gave me everything

To my sisters, my nephews, Moulay El Arabi, Lalla Fatima Zahra, and all the people who help me with advice or payments

**AMMARI MOHAMMED**

First of all, I would like to thank the good

God who brought me to the end

my studies.

I dedicate this work:

To my parents, to my dear mother who gave me everything

To my BROTHERS, and all the people who help me with advice or payments

**DRIS MOHAMMED HICHAM**

## ABSTRACT

### المخلص

الهدف من هذه الدراسة هو دراسة خلايا البيروفسكايت الهجينة القائمة على الرصاص ومحاولة إيجاد حلول بديلة عنه نظرا لسميته. تم عرض عموميات على الخلايا الشمسية انطلاقا من تاريخ ظهور الخلايا الشمسية وكذا أجيالها والمواد المستعملة فيها وخصائصها الكهربائية تطرقنا كذلك لشرح الخالية الشمسية القائمة على البيروفسكايت وذكرنا المواد المستعملة فيها وطرق التوليف في كل حالة من حالات المادة. مررنا بعد ذلك إلى الخلايا الهجينة الهايبرد القائمة على الرصاص وذكرنا خطورته على الإنسان وكذا البيئة والحيوان فأجرينا مقارنة بينه وبين النحاس فوجدنا أن النحاس أفضل بديل ممكن للرصاص انطلاقا من مقارنة خصائصه بخصائص الرصاص

كلمات مفتاحية: بيروفسكايت, هايبرد, الخلايا الشمسية, طرق التوليف

### Résumé

Le but de cette étude est d'étudier les cellules pérovskites hybrides à base de plomb et d'essayer d'y trouver des solutions alternatives du fait de sa toxicité. Des généralités ont été présentées sur les cellules solaires en se basant sur l'histoire de l'émergence des cellules solaires ainsi que leurs générations, matériaux utilisés dans eux et leurs propriétés électriques. Nous avons également discuté de l'explication des cellules solaires à base de pérovskite et mentionné les matériaux utilisés dans celui-ci et les méthodes de synthèse dans chaque cas du matériau. Nous sommes ensuite passés aux cellules hybrides à base de plomb et mentionné son danger pour l'homme ainsi que pour l'environnement et les animaux. Nous avons fait une comparaison entre celui-ci et le cuivre, et nous avons constaté que le cuivre est la meilleure alternative possible au plomb en comparant ses propriétés avec celles du plomb.

**les mots clé:** pérovskites, hybrides, les cellules solaires, les méthodes de synthèse

### Abstract

The aim of this work is to study the lead-based hybrid perovskite cells and try to find alternative solutions to them due to their toxicity. Literature research was presented on solar cells based on their history as well as their generations, materials used in, and their electrical properties. We also discussed the explanation of the perovskite-based solar cell and mentioned the materials used in it and the methods of synthesis in each case. Then, we passed to the lead-based hybrid cells and mentioned their danger to humans as well as the environment and animals. Also, a comparison was made between lead and copper, and we found that copper is the best possible alternative based on the comparison of its properties with the properties of lead.

**Key words :** perovskite, hybrid, solar cells based, the methods of synthesis.

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## List of symbols

|        |                                 |
|--------|---------------------------------|
| PV     | Solar cell or photovoltaic cell |
| PhI    | Photocurrent                    |
| PhV    | Photovoltaic                    |
| P      | Power output by a solar cell    |
| FF     | Form factor                     |
| $\eta$ | Conversion efficiency           |
| MHPs   | Metal halide perovskites        |
| PCE    | Power conversion efficiency     |
| Jsc    | Current density                 |
| Voc    | Open circuit voltage            |

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# General introduction

### General introduction

The search for renewable and non-polluting energy sources is one of the major technological challenges of the 21st century, given the progressive depletion of reserves of fossil fuels, the growing environmental problems linked to the use of these energies and the increase in operating costs. Therefore, the solution to these problems lies in the control of renewable energies and among them, solar energy with photovoltaic conversion, inexhaustible and clean, occupies a prominent place. This form of energy is a direct transformation of solar energy into electric energy. It is basically ensured by silicon solar cells, whose manufacturing is more and more controlled. The main factor that still hinders the use massive impact of this clean energy production process concerns the manufacturing costs considered excessive in the face of fossil or nuclear energies. To this end, the challenge to which answer the photovoltaic industry is to increase the yield ratio physical/economic performance of solar cells, through the introduction of means technologies to improve the conversion efficiency, by using new materials and structures that can increase device performance photovoltaic while reducing manufacturing costs through implementation techniques easy and inexpensive work. Heterojunction photovoltaic cells are obtained by bringing materials with different energy gaps into contact. Among the materials that have attracted a lot of attention are the perovskites in full expansion today, because of the technological importance and promising physical properties these materials offer when applied in photovoltaics (PV). With the sun radiating renewable clean energy and lasting in abundance; using this energy in a profitable and low-cost way is at the same time attractive and challenging for human society. To harvest energy solar, it is important to exploit the known phenomenon, known as the Photovoltaic (PV) effect, in which light is directly converted into electricity.

Hybrid perovskites are very unstable and easily degrade to rather soluble compounds of Pb or Sn with  $K_{SP}=4.4 \times 10^{-9}$ , which significantly increases their potential bioavailability and hazard for human health, as confirmed by recent toxicological studies. Although the 50% lethal dose of lead [LD50(Pb)] is less than 5 mg per kg of body weight, health issues arise at much lower exposure levels. Young children absorb 4–5 times as much lead as adults and are most susceptible to the adverse effects of lead. In 2003, a maximum blood Pb level (BLL) of 5  $\mu\text{g/dL}$  was imposed by the World Health Organization, which corresponds to the amount of Pb

contained in only  $5 \times 5 \text{ mm}^2$  of the perovskite solar module. That's why our thesis is interest to find alternative metals less toxic then Pb and close to his characteristic.

In the first chapter, we will expose generalities on the cells sunscreens, their function principle based on a physical effect which is called the effect photovoltaic. We will also present the evolution of the technology of solar cells which has gone through several generations depending on the structure and material used.

In the second chapter we will making a presentation of perovskite solar cells ,his principal working ,their materials such as  $\text{CaTiO}_3$ ,  $\text{BaTiO}_3$ , and  $\text{NaTaO}_3$  ,then talk about the Synthesis of this materials and we will conclude with the key challenges.

In the third chapter we shall try to mention the large interest of lead halide perovskite in the science community then we will talk about his toxicity at humans, animals, and environment. Then we will mention the using of many metals in perovskite such as tin, antimony, and copper. After that we mention our alternative metal for lead. Finally we will conclude this thesis with general conclusion.

# **Chapter I**

## **GENERAL INFORMATION ON SOLAR CELLS**

The sun is an almost unlimited energy source, it could cover several thousand times our global energy consumption. This is why man has long sought to take advantage of this important energy distributed throughout the planet. He managed to achieve this objective by the means known as photovoltaic cell where the electrical energy coming from a photovoltaic conversion from solar energy has become an essential alternative to other energy sources in the process of depletion such as oil.

In this chapter, we will present generalities on solar cells, starting with a presentation of the photovoltaic cells since it is the basic principle of operation of the solar cell. We will also explain the parameters of the solar cell, as well as the different generations of this cell. We will conclude this chapter with some advantages and disadvantages of photovoltaic energy.

### **I .1 Definition of solar cells**

Solar cell or photovoltaic cell (PV) , any device that directly converts the energy of light into electrical energy through the photovoltaic effect. The overwhelming majority of solar cells are fabricated from silicon with increasing efficiency and lowering cost as the materials range from amorphous (no crystalline) to polycrystalline to crystalline (single crystal) silicon forms. Unlike batteries or fuel cells, solar cells do not utilize chemical reactions or require fuel to produce electric power, and, unlike electric generators, they do not have any moving parts.[1]

### **I .2 First application**

Humanity has always known the power of the sun and it is interesting to observe how the use of energy from the sun has evolved. In reality this energy such as the use of light or the sun is much older. Thousands of years ago, different civilizations honored the sun as a true god. In 212 BC, Archimedes used the sun to stop the Roman fleet using polished bronze mirrors. With these mirrors he succeeded in setting fire to the fleet from a distance. Several decades separated the first specific photovoltaic applications from the technological maturity allowing wide access to electricity.

Here some important dates in the history of photovoltaics [2].

1839: The transformation of sunlight into electric current goes back to this date, the French physicist Edmond Becquerel discovered the process of using sunlight to produce electric current in a solid material. This is the photovoltaic effect.

1875: Werner Von Siemens exhibited before the Berlin Academy of Sciences an article on the photovoltaic effect in semiconductors. But until the Second World War, the phenomenon was still a laboratory curiosity.

1905: Albert Einstein wrote that light could enter the interior of atoms and that the collision between photons and atoms could knock electrons out of their orbits and allow the creation of an electric current.

1912: Albert Einstein will be the first to explain the photovoltaic effect phenomenon, and receives the Nobel Prize in Physics in 1921 for this explanation.

1954: Three American researchers, Chapin, Pearson and Prince, developed a high-efficiency photovoltaic cell at a time when the emerging space industry was looking for new solutions to power its satellites.

1958: A cell with an efficiency of 9% is developed. The first satellites powered by solar cells are sent into space.

1973: The first house powered by photovoltaic cells is built at the University of Delaware.

1983: The first car powered by photovoltaic energy traveled a distance of 4,000 km in Australia.

1995: Grid-tied rooftop photovoltaic programs were launched in Japan and Germany, and have been widespread since 2001.

### **I .3 Different generation of solar cells**

#### **I.3.1 The First generation**

It relates to conventional bulk silicon (c-Si) solar cells with a substrate thickness greater than 100  $\mu\text{m}$ . For its two monocrystalline and multi-crystalline types, the technology of this generation is mature and well mastered. It presents a world production of approximately 84% of the PV market (37% monocrystalline, 2% ribbon and 45% multi-crystalline) [4]. Its yield is in the 15-26% range (Table I-1).

**Table I-1:**First generation solar cells [3-7]

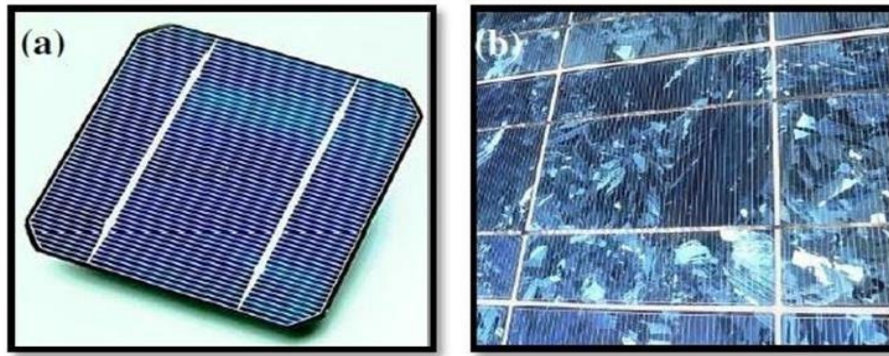
| Solar cell<br>(date)                               | Area(cm <sup>2</sup> ) | yield(%) | test center |
|--|------------------------|----------|-------------|
| <i>Monocrystalline silicon</i><br>0,5<br>(7 /2016) | FhG-ISE <sup>a</sup>   | 180,43   | 26,3 ±      |
| <i>Multicrystalline silicon</i><br>(11/2015)       | FhG-ISE                | 242,74   | 21,3 ± 0,4  |

### I.3.1.1 Historical

In 1921, Albert Einstein received the Nobel Prize of physics for the discovery of the law of the photoelectric effect. This effect describes the emission of electrons when the light is absorbed into a material. It is the basis of the first generation of solar cells that still represent 90% of the market. [34]

### I.3.1.2 Their types

- ❖ **Monocrystalline:** which is prepared by deposition of layers "atom by atom", by epitaxy. It has the advantage of having a very good output (150W/cm<sup>2</sup> in full sun), and a very long lifespan, but of high cost, and low output under low illumination. It finds its applications in solar panels used in the aerospace and military fields.
- ❖ **Polycrystalline:** with yield  $\eta \sim 14$  to 18% (in 2015). It is prepared by heating amorphous Si followed by cooling (crystalline by domain). Its advantage is good performance (at 100W/cm<sup>2</sup> in full sun), cheaper than monocrystalline, but with limited performance under low light. It is found in solar panels now used by almost all individuals where  $\eta \sim 16$  to 24% (2015) [5]



**Figure I.1:** (a) monocrystalline and (b) polycrystalline cells [8-9].

### I.3. 2 Second generation

It concerns thin-film solar cells with a thickness of less than 50  $\mu\text{m}$  using amorphous silicon or III-V compound materials such as gallium arsenide (GaAs), cadmium telluride (CdTe), di-selenide of copper and indium ( $\text{CuInSe}_2$ ) and titanium dioxide ( $\text{TiO}_2$ ). It is possible to reduce the production costs of these types of solar cells compared to the first generation. In addition, they are flexible and their use is more varied. However, the production steps require more energy because vacuum processes and high temperature treatments are used (Table I-2).

**Table ( I-2 ).** Examples of second generation solar cells [7]

| Solar cell<br>(date)                        | Area( $\text{cm}^2$ )                | Yield(%)       | test center |
|---|--------------------------------------|----------------|-------------|
| GaAs  | 0,9927<br>NREL(05/2012) <sup>b</sup> | 28,8<br>$\pm$  | 0,9         |
| CIGS<br>ISE(04/2014) <sup>a</sup>           | 0,9927                               | 21,0 $\pm$ 0,6 | FhG-        |
| CdTe<br>(08/2014)                           | 1,0623                               | 21,0 $\pm$ 0,4 | Newport     |
| Amorphous silicon<br>(07/2014) <sup>c</sup> | 1.001                                | 10.2 $\pm$ 0.3 | AIST        |

#### I.3.2.1 Historical

Thin film cells are well-known since the late 1970s, when solar calculators powered by a small strip of amorphous silicon appeared on the market. They are now available in very



large modules used in sophisticated building-integrated installations and vehicle charging systems. [32]

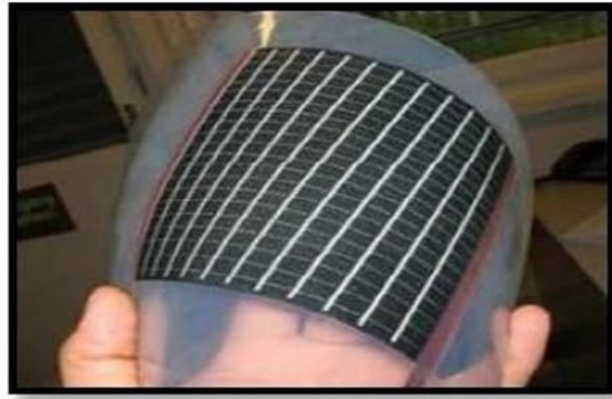
### I.3.2.2 Their types

- ❖ **Amorphous Si cell:** projection of silicon onto glass. This is what is used for watches or calculators. It has the advantage of operating under low illuminance, but expensive and temperature sensitive, low yield and deteriorates rapidly. It is applied to roll-up solar panels.



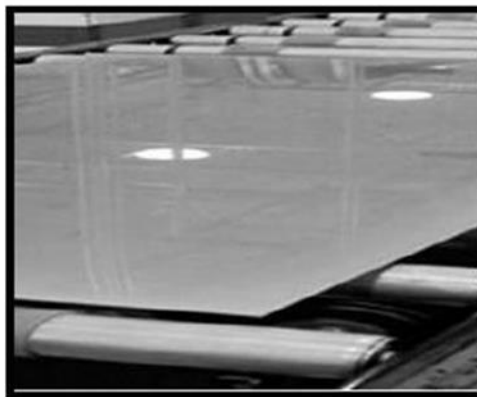
**Figure I.2:** Amorphous silicon cell [8]

- ❖ **Tandem cell:** prepared from a mixture of crystalline Si and amorphous Si absorbing in different spectral domains. It has the advantage of good efficiency (29%) and high sensitivity over a wide range of wavelengths, but has the disadvantage of very high cost. It is applied to wide-spectrum, high-efficiency solar panels, especially in aerospace [8].
- ❖ **CIS cell:** CIS cells are very promising materials for PV conversion with a band gap of 1 eV (Figure I.3). However, the partial substitution of indium atoms by gallium atoms makes it possible to increase the band gap value up to 1.7 eV. The record efficiency obtained with the CIGS material is 20.4% [11].



**Figure I.3:** CIGS cells [12]

- ❖ **CdTe cell:** the first solar cell based on CdTe was manufactured mainly by the company “First Solar” (Figure I.4). A record yield of approximately 21.5% was obtained in February 2015. However, the presence of cadmium, which is a toxic material, and the scarcity of tellurium risk severely limiting their development despite a very interesting yield [11].



**Figure I.4:** CdTe cells [8-15].

### **I.3.3 Third Generation**

Research to improve the performance of solar cells by improving its efficiency led to the development of the third generation of solar cells[14]. This technology suffers from poor electrical performance (technologies not semiconductors including polymer-based cells).

#### **I.3.3.1 Historical**

The generation’s history back to the first year of the 1990s. The superiority of this generation is their flexibility compared to other generations. [35]

### I.3.3.2 Their types

- ❖ **Organic cells:** This type of cell consists of an active layer, which in turn consists of several layers of polymer (Figure I.4). This active layer is sandwiched between two conductive layers. Generally, one of these layers is transparent with a thickness not exceeding 10 nm. They are still at the research stage with yields not exceeding 5% [15].



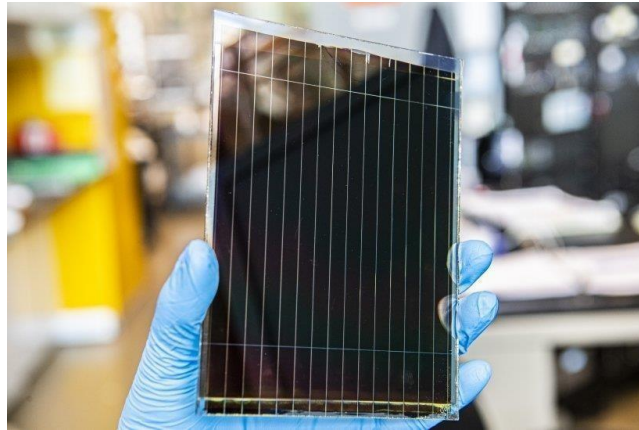
**Figure I.5:** Organic solar cells [16].

- ❖ **Multi-junction cells:** which are prepared from a mixture of crystalline Si and other semiconductors absorbing in different spectral ranges. They have the advantage of having excellent efficiency (42%, 2015) and very high sensitivity over a wide range of wavelengths, but have the disadvantage of extremely high cost, although they are applied to high-efficiency, spread-spectrum solar panels used in the aerospace and military fields [17].
- ❖ **Dye solar cells (from Grätzel):** They were developed in the early 90s by Professor Grätzel and his research team, inspired by the phenomenon of photosynthesis. They are characterized by their simple manufacture, their long life and their stability over the years. Currently, this type of cell represents a yield of 10.4% in the laboratory obtained by the Sharp company [15,18,19].

### I.3.4 Fourth-generation

Solar cell technology is also referred to as the 4G solar cell technology. The 4G solar cells are engineered at solar scale and are characterized by the flexibility of conducting polymer films, and the stable nanostructures.

The essence of the nanomaterials in these solar cells enables large volume of surrounding the nanomaterial to be filled using a conductor, such as a polymer [31] A perovskite solar cell is a type of solar cell which includes a perovskite-structured compound, most commonly a hybrid organic-inorganic lead or tin halide-based material, as the light-harvesting active layer [32].



**Figure I.6:** Perovskite cell. Photo courtesy of Dennis Schroeder / National Renewable Energy Laboratory. [37]

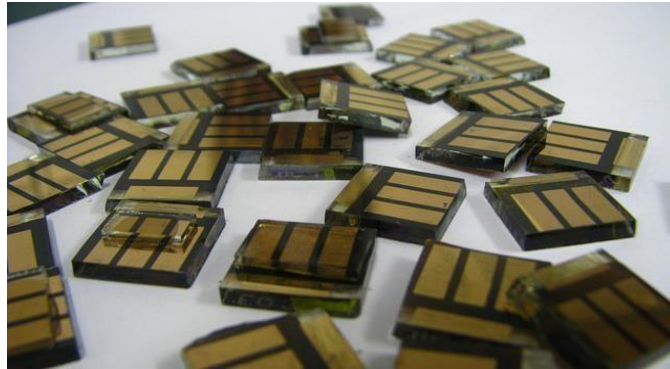
#### **I.3.4.1 Historical**

In 2012, Professor Henry Snaith discovered perovskite semiconductor material and used it in solar cells, and this field became the center of attention of all researchers in this field in the world, because perovskite is one of the best materials discovered by mankind in its physical properties and electrical conductivity that made it superior to silicon. In efficiency, because silicon cells suffer from crystal defects that detract from their efficiency of conduction. [36]

#### **I.3.4.2 Their types**

- ❖ **Hybrid organic-inorganic perovskite solar cells:** are mixes of nanostructures of both organic and inorganic materials. Therefore, they combine the unique properties of inorganic semiconductor nanoparticles with properties of organic/polymeric materials. In addition to this, low cost synthesis, process ability and versatile manufacturing of thin film devices make them attractive. Also, inorganic semiconductor nanoparticles may have high absorption coefficients and particle size induced tunability of the optical band-

gap. Thus, the organic/inorganic hybrid concept for photovoltaic solar cells is getting interesting and attractive in recent years. [33]



**Figure I.7:** Hybrid organic-inorganic perovskite solar cells [38]

- ❖ **Thin halide perovskite:** A tin-based perovskite solar cell is a special type of perovskite solar cell, where the lead is substituted by tin. It has a tin-based perovskite structure, where 'A' is a 1+ cation and 'X' is a monovalent halogen anion. [32]



**Figure I.8:** A thin film of 2D halide perovskite crystals of uniform thickness [39]

#### **I.4 Materials used in solar cells**

Special materials are used for the construction of photovoltaic cells. These materials are called semiconductors. The most commonly used semiconductor material for the construction of photovoltaic cells is silicon. Several forms of silicon are used for the construction; they are single-crystalline, multi-crystalline and amorphous. Other materials

used for the construction of photovoltaic cells are polycrystalline thin films such as copper indium diselenide, cadmium telluride, and gallium arsenide.[20]

- **Silicon**A number of the earliest photovoltaic (PV) devices have been manufactured using silicon as the solar cell material and it is still the most popular material for solar cells today. The molecular structure of single-crystal silicon is uniform. This uniformity is ideal for the transfer of electrons efficiently through the material. However, in order to make an effective photovoltaic cell, silicon needs to be "doped" with other elements. Multi-crystalline silicon is normally considered less efficient than single-crystal silicon. On the other hand, multi-crystalline silicon devices are less expensive to produce. The casting process is the most common means of producing multi-crystalline silicon on a commercial scale. Amorphous silicon can absorb 40 times more solar radiation than single-crystal silicon. This is one of the main reasons why amorphous silicon can reduce the cost of photovoltaic. Amorphous silicon can be coated on low-cost substrates such as plastics and glass. This makes amorphous silicon ideal for building-integrated photovoltaic products.[20]
- **Polycrystalline thin-film** are formed in a wide variety of thin-film deposition processes including chemical vapor deposition, physical vapor deposition, and sputter deposition. A variety of models are being developed to study and simulate the evolution of the surface morphology and thin-film microstructure during growth. Both continuum and discrete models are being studied. Topics of current interest include the effects of nucleation and substrate roughness on the average grain size and grain-size distribution, the effects of ion-erosion on faceting and on thin-film quality, and the development of improved mathematical methods for characterizing surface morphology.[21]
- **Copper Indium Diselenide**CIS for short, has an extremely high absorptivity. This means that 99% of the light illuminated on CIS will be consumed in the first micrometer of the material. The addition of a small amount of gallium will improve the efficiency of the photovoltaic device.[20]
- **Cadmium Telluride**is a direct-band gap material with band gap energy that can be tuned from 1.4 to 1.5 (eV), which is nearly optimal for converting sunlight into electricity using a single junction.[22]
- **Gallium Arsenide**(GaAs) is a compound built from the elements gallium and arsenic. It is often referred to as a III-V compound because gallium and arsenic are in the III group and V group of the periodic table, respectively. [23]

- **Perovskite materials** structured materials used in solar cells are generally hybrid organic-inorganic lead or tin-halide materials, such as methylammonium lead halide. These materials can be solution-processed, hence enable inexpensive and simple fabrication. The efficiency of perovskite-based solar cells has been steadily increasing and is reported to be more than 20% in the lab currently. One of the key advantages of these materials is their ability to absorb sunlight across the entire visible spectrum.[20]
- **Quantum dots** are tiny semiconductor particles. They can be composed of different types of atoms: cadmium, selenium, copper, zinc... In all cases, the Quantum Dot constitutes an enclosure in which are confined one or more electrons, or one or more holes (electronic gaps). [24]
- **Organic/polymer materials** such as polyphenylene vinylene and small organic small molecules such as phthalocyanines, polyacenes, and squarenes are also used in solar cells. These highly conjugated organic molecules have a broad absorption in the visible and near infrared region. These materials are deposited as thin films either by vacuum deposition methods or solution processing, and solar cells using these materials are usually thin and flexible. [25]
- **Dye solar cells (DSCs)** they are also called dye sensitized solar cells (DSSC) or Grätzel cells named after the Swiss chemist Michael Grätzel who was greatly involved in the development of new cell types.[26]

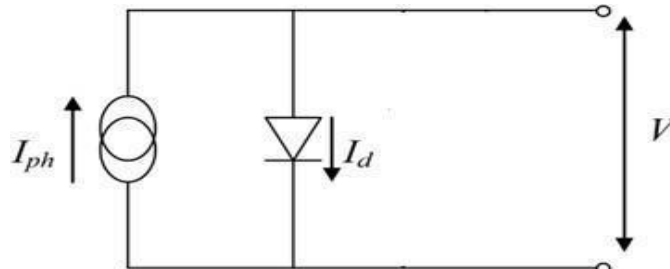
### I.5 Efficiency of a Solar cell

Simply the amount of electrical power coming out of the cell compared to the energy from the light shining on it, which indicates how effective the cell is at converting energy from one form to the other. The amount of electricity produced from PV cells depends on the characteristics (such as intensity and wavelengths) of the light available and multiple performance attributes of the cell.

An important property of PV semiconductors is the bandgap, which indicates what wavelengths of light the material can absorb and convert to electrical energy. If the semiconductor's bandgap matches the wavelengths of light shining on the PV cell, then that cell can efficiently make use of all the available energy.

### I.6 Electrical parameter of solar cells

The parameters of the solar cell are linked to the model of the solar cell. It is considered that an ideal solar cell is equivalent to a perfect diode with a current source connected in parallel as shown in the following figure:



**Figure I.9:** Equivalent diagram of the ideal solar cell.

#### I.6.1 Photocurrent $I_{ph}$

This is the current for which the voltage across the terminals of the cell or the PV generator is zero. In the ideal case (zero, infinite), this current merges with the photo current  $I_{ph}$ .

#### I.6.2 Photovoltaic $V_{ph}$

This is the voltage for which the current delivered by the PV generator is zero (the maximum voltage of a solar cell or a PV generator). Its expression is deduced from the following equation:[30]

$$0 = I_{ph} - I_0 \left[ e^{\frac{V_{co}}{V_T}} - 1 \right] - \frac{V_{co}}{R_{sh}}$$

In the ideal case ( $R_s \rightarrow 0, \rightarrow R_{sh} = \infty$ ) we obtain:

$$V_{co} = V_T \ln\left(\frac{I_{ph}}{I_0} + 1\right)$$

#### I.6.3 Power output by a solar cell, P

The output power P of a solar cell is given by:

$$P = I \cdot V$$

Which means current times voltage [29]



### I.6.4 Form factor, FF

The FF form, also known as fill factor, it is defined by:

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}}$$

This factor shows the deviation of the curve  $I = f(V)$  from a rectangle (of length  $V_{oc}$  and width  $I_{sc}$ ) which corresponds to the ideal solar cell [30]

### I.7 Conversion efficiency $\eta$

The solar cell conversion efficiency is an indicator that expresses how much of the incident light can be converted into electrical energy. This conversion efficiency can be represented as a fraction with the power of the incident light in the denominator and the electrical power obtained from the solar cell in the numerator[28]

$$\text{Conversion efficiency (\%)} = \frac{\text{Generated electrical power(W)}}{\text{Incident light power(W)}} \times 100$$

### I.8 Advantages and disadvantages

Solar cells have many advantage and disadvantage We mention among them[27]

#### I.8.1 Advantages

- **Renewable Energy:** The most obvious advantage of solar cells is that they use solar energy, which is a renewable energy source.
- **Economy-friendly Energy:** The other benefit of using solar cells is that they provide a great opportunity to create savings on your electric bill since you do not pay for the energy that you generate
- **Environmentally Friendly Energy:** With solar cells occurs almost no pollution, and this is a great advantage.
- **Innovative Energy:** Photovoltaic is a popular topic in green energy and is considered to be a good solution to prevent climate change.

- Long Term Energy: PV systems often have a long life and good durability. At the same time, there is often a guarantee of at least 20 years on your PV panels, making it a reliable electricity source on your roof
- Selling Energy: If your home has solar cells, it is often easier to sell the property at a higher price. In the UK, there are some grants and incentives available if you want to invest in solar cells.
- Infinite Energy: When you have the opportunity to extract energy from sun rays, this is a source of energy that will never be exhausted; therefore, this is an innovative market under continuous research and development.

### **I.8.2 Disadvantages**

- High Investment: One of the most important disadvantages of solar cells is the relatively high installation cost of solar panels. For example, the estimated cost of a 5kW solar PV system is around £7000 - £9000, depending on your roof type and other conditions.
- Interior Needs: Not all households can satisfy their requirements and get the optimum out of their solar cells yet. Solar cells are very sensitive in terms of their location, which means that if there is shade on your lot, it is difficult to exploit solar installation optimally
- Seasonal Energy: Compared to other types of renewable energy, the solar power plant is highly seasonal, since we can have periods of limited sun.
- Solar Cells on Your Accommodation: It might be harder to install solar panels on older households, as they often have different designs that can provide shade.

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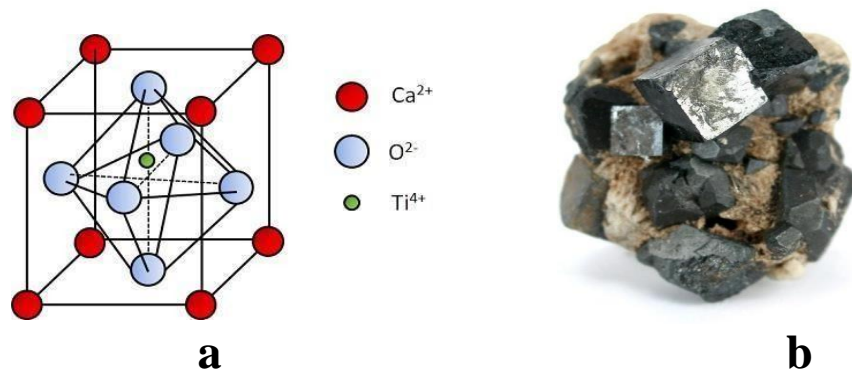
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**CHAPTER II**

**PEROVSKITE SOLAR CELLS**

The general chemical formula of a perovskite material is  $ABX_3$ , which contains a crystal structure similar to  $CaTiO_3$ . It was initially discovered by German geologist Gustav Rose in 1839 in Ural Mountains, and named after Russian mineralogist Lev Perovski. In  $ABX_3$  perovskite, A and B are termed as metal cations having ionic valences combined to +6, e.g., ( $Li^+ : Nb^{5+}$ ;  $Ba^{2+} : Ti^{4+}$ ;  $Sr^{2+} : Mn^{4+}$ ;  $La^{3+} : Fe^{3+}$ ) and X is an electronegative anion with ionic valence  $-2$  such as  $O^{2-}$ ,  $S^{2-}$  etc. . The perovskite materials may be oxides, halides, nitrides, sulfides, etc., and they may exist in different forms, such as powders, thin films, etc. The perovskite material has attracted our attention as it can house up a variety of cations at A- and B-sites individually and/or simultaneously along with anions at X-site . The perovskite materials can be classified in ideal and distorted perovskite materials.[1]

In this chapter, we will study the two single and double perovskite materials most commonly used in optoelectronics, their different crystalline structures, device evaluation and key challenges.



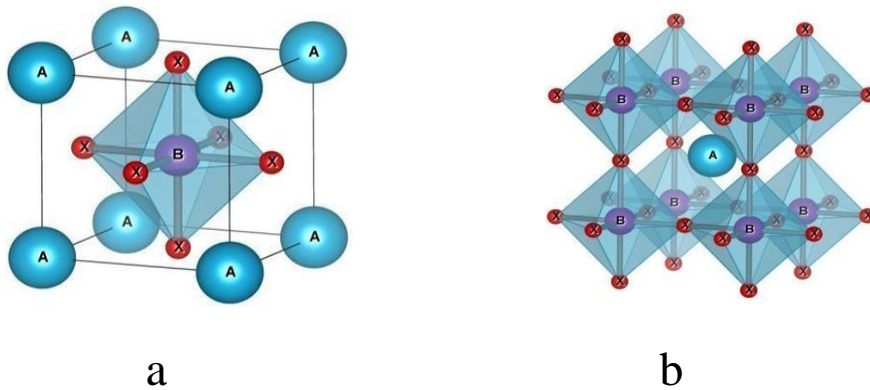
**Figure II.1** a) Crystal structure of  $CaTiO_3$  perovskite, b) Perovskite material  $CaTiO_3$

## II .1 Perovskite materials

Chemically, perovskites (prototype  $CaTiO_3$ ) with general formula  $ABX_3$  consist of three sites (two cationic sites A and B, and an anionic site X). Site A (cation A) is occupied by cation(s) of high ionic radius ( $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Pb^{2+}$ ,  $Bi^{2+}$ ). Site B (cation B) compared to site A is occupied by ions ( $Ti^{4+}$ ,  $Zr^{4+}$ ,  $Fe^{3+}$ ,  $Sc^{3+}$ ). The X anions are usually the oxygen ion  $O^{2-}$  or fluoride  $F^{2-}$ .



Figure II.2.(a) represents the unit cell structure of  $ABX_3$  perovskite, the positions of atoms A, B and X are: A (0.0.0), B (1/2, 1/2, 1/2) and X1(1/2, 1/2, 0), X2 (1/2, 0, 1/2) and X3 (0, 1/2, 1/2). In addition, the unit cell of the perovskites in this structure contains 5 atoms (one atom of cation A, one atom of cation B and three oxygen atoms), so it is a compact assembly where the compactness, which is the proportion of space occupied by the atoms of the lattice of this structure (cubic with centered faces) is 74%.



**Figure. II.2:** Two different ways to represent the cubic  $ABX_3$  perovskite structure.

a) atom B at the origin (BX<sub>6</sub> octahedron shown), b) atom A at the origin of the cell

Depending on the occupation of sites A and B, two types of perovskites can be defined:

- **Simple perovskites:** these are the perovskites for which the site A and the site B are occupied by a single type of atom, we can cite for example the compounds:  $CaTiO_3$ ,  $BaTiO_3$ ,  $NaTaO_3$ ,  $PbTiO_3$ ....
- **Complex Perovskites:** where sites A and/or B are occupied simultaneously by at least two different cations, case of compositions  $(1/2Na1/2Bi)TiO_3$ ,  $Pb(1/3Mg2/3Nb)O_3$ ,  $(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_3$ , for example. This category encompasses solid solutions between several compounds with a perovskite structure (simple or complex), where there may be an order in the arrangement of cations within the structure [3].

## II .2 Synthesis of perovskite materials

As we know that the physical, chemical, and optical properties of the perovskite materials are strongly synthesis route dependent. One has to choose a suitable

synthesis method to obtain the desired properties from the prepared materials. Synthesis techniques also affect crystal structure and morphology of the samples [4]. The synthesis techniques can be divided into three main classes as given below:

- ❖ Solid-state synthesis
- ❖ Liquid-state synthesis
- ❖ Gas-state synthesis

These techniques have their own advantages. Solid-state methods are used to synthesize bulk materials, while liquid-state techniques are used to produce nanomaterials. However, gas-state methods are mostly used to fabricate thin films.

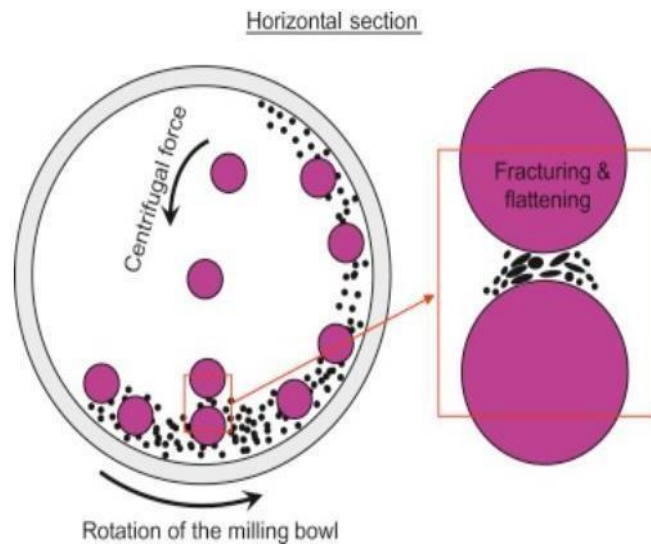
### **II.2.1 Solid-state synthesis**

Solid-state synthesis technique is used to produce polycrystalline materials. It is also known as ceramic method because most of the ceramics are synthesized by this method. This is most widely used technique by researchers. These method requires raw materials in carbonates and/or oxides forms. In this method, the raw materials do not react chemically to each-other at room temperature. When the mixture of raw materials is heated at very high temperatures (i.e., 700–1500°C), the chemical reaction takes place at significant rate. we use two methods in this technique:

- **Mechanical ball-milling method:** Ball milling is a size reduction technique that uses media in a rotating cylindrical chamber to mill materials to a fine powder. As the chamber rotates, the media is lifted up on the rising side and then cascades down from near the top of the chamber. With this motion, the particles in between the media and chamber walls are reduced in size by both impact and abrasion. In ball milling, the desired particle size is achieved by controlling the time, applied energy, and the size and density of the grinding media. The optimal milling occurs at a critical speed. Ball mills can operate in either a wet or dry state. While milling without any added liquid is commonplace, adding water or other liquids can produce the finest particles and provide a ready-to-use dispersion at the same time. Grinding media comes in many shapes and types with each having its own specific properties and advantages. Key properties of grinding media include composition, hardness, size and density. Some common types include alumina, stainless steel,

yttria stabilized zirconia and sand. Ball milling will result in a ball curve particle size distribution with one or more peaks. Screening may be required to remove over or undersized materials.

- High energy ball-milling method: The synthesis of materials by high-energy ball milling of powders was first developed by John Benjamin (1970) and his coworkers at the International Nickel Company in the late 1960s .It was found that this method, called mechanical alloying, could successfully produce fine and uniform dispersions of oxide particles ( $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{ThO}_2$ ) in nickel-base superalloys which could not be made by conventional powder metallurgy methods .It is a ball milling process where a powder mixture placed in the ball mill is subjected to high-energy collision from the balls. Fig. II.3 shows the motions of the balls and the powder. Since the rotation directions of the bowl and balls are opposite, the centrifugal forces are alternately synchronized. Thus, friction resulted from the hardened milling balls and the powder mixture being ground alternately rolling on the inner wall of the bowl and striking the opposite wall. The impact energy of the milling balls in the normal direction attains a value of up to 40 times higher than that due to gravitational acceleration. Hence, the planetary ball mill can be used for high-speed milling [12].



**Figure.II.3:** Schematic view of the motion of the ball and powder mixture.

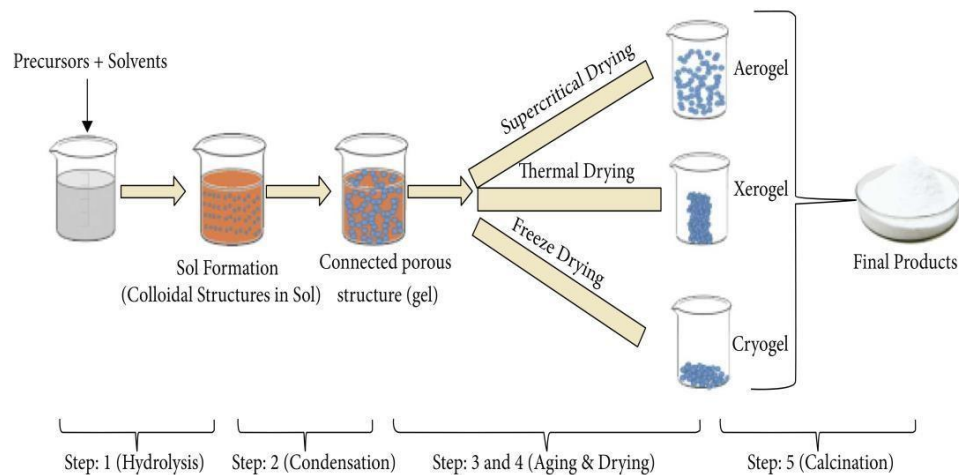
### II.2.2 Liquid-state synthesis technique

The liquid-state synthesis technique is a method of synthesis of nanomaterials. It is most widely used by researchers and scientists for the production of nanoparticles of the oxide materials. In this method, the raw materials may be in the form of nitrates, acetates or oxalates, which may react to each other at an ordinary temperature. Auto-combustion, sol-gel, co-precipitation, etc. are different liquid-state synthesis techniques used for the preparation of perovskite nanomaterials.

There are three methods in this technique:

- Auto-combustion method: The auto-combustion synthesis method is a low-cost and very facile technique for the production of perovskite nanomaterials. In this technique, the starting materials are used in oxalates and/or acetates and/or nitrates forms, which are easily soluble in de-ionized water. It involves some organic fuel, such as urea, citric acid, and glycine to assist the combustion.[1]
- Sol-gel method: The sol-gel process is a more chemical method (wet chemical method) for the synthesis of various nanostructures, especially metal oxide nanoparticles. In this method, the molecular precursor (usually metal alkoxide) is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis/alcoholysis. Since the gel obtained from the hydrolysis/alcoholysis

process is wet or damp, it should be dried using appropriate methods depending on the desired properties and application of the gel.[13]



**Figure.II.4.** Schematic of different stages of sol-gel process: from precursor to aerogel

- Co-precipitation method: The co-precipitation method is also one of the methods used of the production of nanomaterials. This method needs raw materials of metal cations from a general medium and precipitates in the form of oxalates, carbonates, citrates or hydroxides. The solubility of the used compounds should be very close to each other for a proper precipitation. The controlling pH of the precursor solution, stirring speed, concentration, and temperature of the mixture are important parameters for the co-precipitation method.[1]

### II.2.3 Gas-state synthesis technique

Gas phase nanoparticle preparation methods have attracted huge interest over the years due to number of benefits that they can deliver over other methods. These techniques are typically characterized by the ability to accurately control the process parameters to be able to tune shape, size and chemical composition of the nanostructure. Although, means and methods can differ, almost all gas phase nanomaterial production methods follows following sequence

- Suspending the precursor materials in a gas phase
- Transforming the precursor material to small clusters
- Enforcing the growth of these clusters to ananoparticles

- Method to collect prepared nanoparticles.[4]

### II .3 Perovskite solar cell

Solar energy, along with wind, biomass, tidal and geothermal energy are emerging as alternative energy sources for our energy-starved planet. Among these sources, solar energy is a renewable and clean energy that provides an answer to the growing concerns about global warming and greenhouse gases from fossil fuels. In some parts of the world, this energy is supplied to the grid at costs competitive with fossil fuels. This has resulted in the availability of commercial products from this range of solar cells for select consumers in power electronics and low energy applications in buildings .[5]

Recent advances in the assembly of standard silicon solar cells have ensured the integration of photovoltaics into the mainstream energy mix, with a recent forecast predicting that one-third of global electricity demand will be met by photovoltaic by 2030 .[6]

### II .4 Perovskite solar cell principal

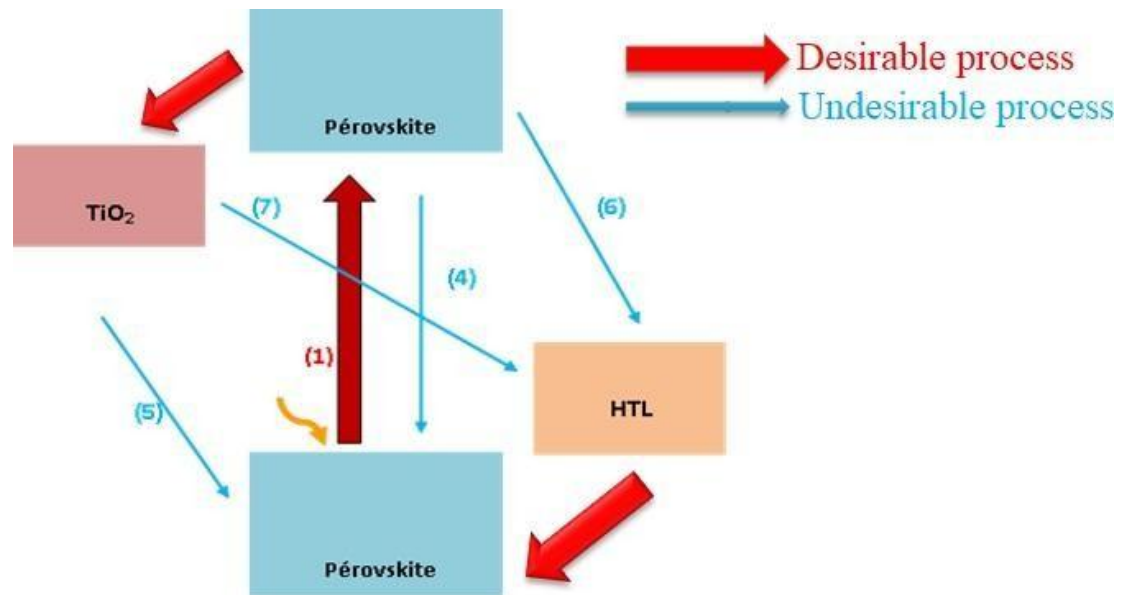
A simplified operating principle of the perovskite-based solar cell involves the absorption of photons by the perovskite absorber layer. The perovskite absorber has a low exciton binding energy which indicates the generation of free charge carriers upon photon absorption and occurs within picoseconds. These generated free charge carriers are then transported to the interface contacts [7]. During the course of the transfer (figure II. 3), the desired process (red arrow) takes place in three stages:

- Photo-excitation in the perovskite absorber
- Electron transfer in the ETL
- Transfer of holes in HTL (or equivalent transfer of electrons from HTL to perovskite)

A large number of unwanted processes (green arrow) can occur. They consist of:

- A recombination of photo-generated species (4)
- A back charge transfer at the interfaces of HTL and TiO<sub>2</sub> with perovskite(5, 6)
- A direct contact between HTL and TiO<sub>2</sub> (7)

Eventually, after overcoming the extraction barriers at the interfaces, the remaining charge carriers can be transferred through selective contact interfaces and can be extracted by the respective electrodes [8].



**Figure II.5.** Diagram of electron transfer and recombination processes in perovskite-based solar cells

## II .5 Device evaluation

PVSCs strongly depend on the composition of perovskite, hole transport materials, electron transport materials, and their interfaces. The evaluation of PVSC devices depends on the roughness of the interface, the cost of the devices, PCE values, and stability. When PVSCs were introduced to the world they were highly unstable and PCE values were very low. However, progress in PVSCs happened when the electrolyte-based hole transport layer was replaced by spiro-MeOTAD, a solid-state material. This increased the stability as well as PCE values of PVSCs. Instead of using a single halide in perovskite materials, a mixed halide  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  composition was used. It was observed that PCE values and stability increased. Furthermore, modification of the nanoporous layer, which replaced conducting material ( $\text{TiO}_2$ ) with nonconducting material ( $\text{Al}_2\text{O}_3$ ), improved the open-circuit voltage of PVSCs, which increased the PCE to 10.90%. Later, it was shown that the performance of PVSC devices increased for  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$  mixed halide perovskites.

The result was that efficiency increased for lower concentrations of Br, and for higher concentrations perovskite films provided better stability against humidity. Subsequently, PVSCs researchers tried to change deposition methods instead of single-step deposition they used two-step deposition for perovskite films, which improved their morphology. The efficiency of further increased when solvent deposition was replaced by thermal evaporation and  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  mixed perovskite. The observed efficiency for this was 15.40%. Further increase in efficiency of PVSC devices was reported for poly (triarylamine) as a hole transport material and  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$  mixed halide perovskites. There followed a further modification in deposition technique, and cations of larger radii were used, which had a symmetrical cubic phase and increased the  $t$  factor. This modification improved the devices. Researchers also tried different proportions of inorganic cations and halide anions in mixed perovskite, which allowed their properties to be tuned [9].

## II .6 Key challenges

Despite having potential to replace silicon based solar cell, with low cost fabrication and high device efficiency, perovskite solar cells also faces some major challenges. Material toxicity, device hysteresis, and perovskite material stability are major challenges which need to be overcome for it be commercialized on a wide scale. Use of toxic lead in perovskite is a matter of environmental concern. Ongoing efforts aim to find a replacement for toxic lead. Apart from toxicity, long term stability of perovskite solar cells is a major bottleneck in achieving its high potential. These high efficiency organic-inorganic hybrid perovskite solar cells are highly sensitive to moisture in ambient air. Moisture leads to a domino effect of decomposition of perovskite film causing material degradation, thus losing photovoltaic property. Temperature is also an important factor for perovskites as it leads to decomposition at high temperatures ( $>90$  °C). Hysteresis phenomenon in perovskite material is another critical issue, which has been studied and addressed widely. Various methods have been adopted to reduce the hysteresis behavior in these devices.[10]



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**CHAPTER III**

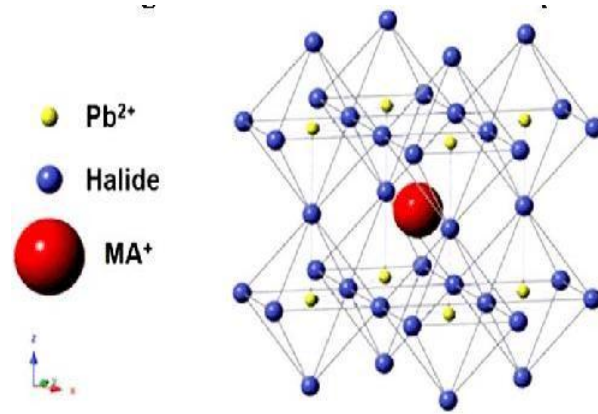
**LEAD HALID PEROVSKITE-  
BASED SOLAR CELLS**

Lead halide perovskites have recently emerged as promising absorbers for fabricating low-cost and high-efficiency thin-film solar cells. The record power conversion efficiency of lead halide perovskite-based solar cells has rapidly increased from 3.8% in 2009 to 22.1% in early 2016. Such rapid improvement is attributed to the superior and unique photovoltaic properties of lead halide perovskites, such as the extremely high optical absorption coefficients and super-long photogenerated carrier lifetimes and diffusion lengths that are not seen in any other polycrystalline thin-film solar cell materials. In the past a few years, theoretical approaches have been extensively applied to understand the fundamental mechanisms responsible for the superior photovoltaic properties of lead halide perovskites and have gained significant insights [1]. In This chapter we highlight the using of pb in lead halide perovskite materials over the years and his properties,improvement attempts, the Possible alternatives ,the using of cu perovskite, then comparison between pb and cu and we conclude with general conclusion .

### **III .1 Presentation of lead halide perovskite-based solar cells**

Metal halide perovskites (MHPs) are an unconventional family of crystalline materials with continuously expanding compositional and structural spaces. These materials intrinsically possess soft crystal lattices that not only contribute to unusual internal carrier dynamics but also lead to their facile interaction with the external environment (matter, light, temperature, electric field, etc.). Since the first report of using MHPs for efficient solar energy harvesting, the scientific field has witnessed an enduring blooming of energy sciences related to MHPs, which have been imparting profound technological impacts on and beyond solar power optimization. Technical discussions on the progress of this exciting energy research have been regularly held in the form of MHPs-focused symposia within the semi-annual Materials Research Society (MRS) meetings, which represent a hub for the growing MHP research community [2]

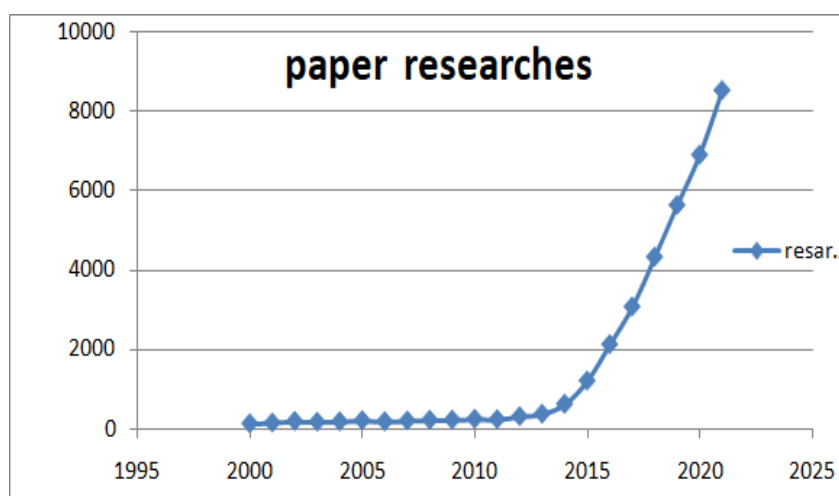
Intense research on the metal halide perovskites (MHPs) in the last few years' streams owing to the tremendous performances obtained for light harvesting and generation. Generally, MHPs contain chemical formula of  $ABX_3$ , where A is a monovalent cation ,B is a divalent cation and X is a halide. The corner sharing  $BX_6$  octrahedra are repeated in all three dimensions (3D) to form the crystal structure within which A cation occupies the voids.[3]



**FigureIII.1.**Crystal lattice of the methylammonium lead halide ( $\text{CH}_3\text{NH}_3\text{-PbX}_3$ ) perovskite structure.

### III .2 Using of Pb in halide perovskite over the years

With the rapid development of industry and economic growth, the global demand for energy is increasing. Because of the limited resources of fossil fuels and the environmental hazards of their combustion products, countries have committed to the development and utilization of new energy. In 2009, Miyasaka and co-workers took the first step in the application of the perovskite structure of  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  and  $\text{CH}_3\text{NH}_3\text{PbI}_3$  as a visible light sensitizer with certified photoelectric conversion efficiency (PCE) of 3.8%. After that, perovskite solar cells (PSCs) became a hot topic of research in the field of photoelectric conversion because of its cost-efficiency and simple manufacturing process.[4]

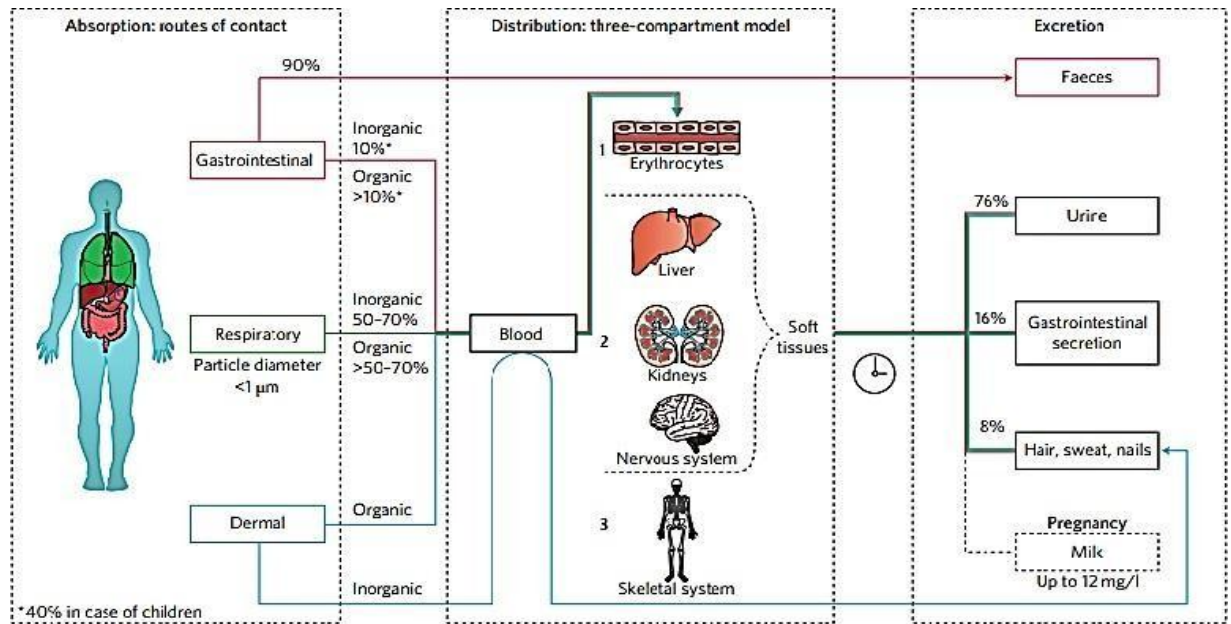


**FigureIII.2.** Number of paper researches in terms of years

As we can see in the curve, there is a large interest in lead-based halide in terms of years and this is due to its great characteristics, among which we mention it has garnered much interest as efficient light harvesters, but also in applications such as light-emitting diodes, lasers, and photodetectors, in view of their favorable intrinsic properties, such as ambipolarity, high charge-carrier mobilities, high diffusion lengths, and high absorption coefficients. Brisk and impressive achievements have brought perovskite solar cells to a level near silicon photovoltaics in terms of efficiency (at least on a laboratory scale) [2], but it is still not green enough.

### III.3 Toxicity of Pb

The toxicity of  $\text{Pb}^{2+}$  is a primary concern for the wide-scale implementation of halide-perovskite absorbers. Lead is a potent human and environmental toxin. Even low exposure levels have been associated with significant health problems including nerve damage, renal failure, and impaired brain development. Lead's toxicity primarily arises from its ability to inhibit key antioxidant enzymes, such as glutathione reductase, by forming covalent attachments to the active-site thiol groups. The neurological effects of lead poisoning arise from its ability to replace  $\text{Ca}^{2+}$  in various signaling proteins (e.g., protein kinase C), interfering with signal transduction throughout the central nervous system. A recent study assessing the potential risks of lead contamination over the lifecycle of a hypothetical perovskite solar module concluded that their commercialization would require a fail-safe encapsulation method that would contain toxic species even in the event of a catastrophic accident. Significant effort would also be required during the manufacturing and decommissioning phase of the module lifecycle to ensure worker safety and prevent environmental contamination. These safety concerns are more acute for the lead perovskites than for older technologies such as CdTe largely because  $\text{PbI}_2$  is water-soluble (the  $K_{sp}$  value for  $\text{PbI}_2$  at 25 °C is  $9.8 \times 10^{-9}$ , amounting to ca. 620 mg of  $\text{PbI}_2$  in 1 L of water) and therefore environmentally mobile, which prevents easy containment and cleanup in the event of accidental release. This problem is likely common to all materials containing toxic elements that can be deposited from solution because high solubility, particularly in polar solvents, enables easy extraction of the material into the environment by water. Therefore, identifying less toxic materials that mimic the optoelectronic properties of the lead-halide perovskites would constitute a major advance in this field.[7]



**Figure III.3.** Schematic overview of absorption, distribution and excretion of Pb compounds in the human body

The percentage indicates the overall amount that can be absorbed. Pb not absorbed upon gastrointestinal intake leaves the body via the faeces (as indicated); Pb not absorbed by respiratory or dermal routes is assumed to have left the body directly by exhalation or to have lost contact through natural body movement, respectively (not indicated in the figure). Pb resides in all of the three compartments with a certain organ-specific retention time, after which it is excreted from the body.

The rise and commercialization of perovskite solar cells (PSCs) is hindered by the toxicity of lead present in the perovskites used as the solar light absorber. To counter this problem, lead (Pb) can be fully (lead-free) or partially (lead-less) replaced by diverse elements. The former compounds suffer from poor efficiency and poor stability, whereas the latter appear more promising. [6]

There are many proposed materials that can replace lead. In this study we mentioned three of them, such as tin (Sn), germanium (Ge), bismuth (Bi), antimony (Sb) and copper (Cu).

### III.4 Using of Sn in perovskite

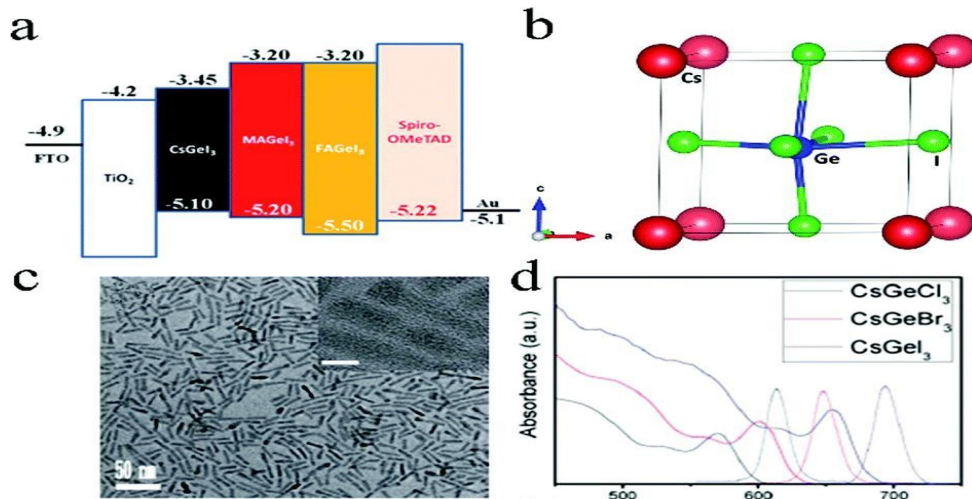
Sn, a Group 14 element with an electronic structure similar to lead, has been firstly considered as the alternative metal for halide perovskite materials. In addition, Sn-based perovskites exhibit a narrower bandgap than their Pb analogues with low exciton binding

energies and longer carrier diffusion lengths. 49,50 Therefore, Sn-based perovskites are regarded as promising light absorbers in optoelectronic applications. Considerable efforts have been devoted toward formulating Sn-based perovskites over the past few years. Snaith and coworkers reported lead-free  $\text{MASnI}_3$  perovskite solar cells with PCE of over 6%. fabricated 2D perovskite  $2\text{SnI}_4$  in flexible photoconductors with excellent photoresponsivity of  $16 \text{ A W}^{-1}$  and detectivity of  $1.92 \times 10^{11} \text{ Jones}$  under 470 nm illumination. However, Sn-based perovskites are sensitive toward moisture and oxygen owing to the oxidation process of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ . [8]

### III.5 Using of Germanium in perovskite

Ge, another Group 14 element, was also considered as a potential candidate for Pb substitution in halide perovskites. The structural and electronic properties of  $\text{MAGeX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) were investigated by theoretical calculations. The results revealed that  $\text{MAGeI}_3$ -based perovskites exhibited similar hole and electron conductive behaviors, stabilities, and optical properties as those of  $\text{MAPbI}_3$ . This indicated that Ge was a competitive alternative to Pb for use in perovskites.  $\text{AGeI}_3$  ( $A = \text{MA}, \text{FA}, \text{Cs}$ ) was prepared by Krishnamoorthy *et al.* (Fig.III.4a) shows the band structure of three perovskites. Among them,  $\text{CsGeI}_3$  (Fig.III.4b) exhibited the highest thermal stability (up to  $350 \text{ }^\circ\text{C}$ ) when compared with the other two Ge-based perovskites. However, solar cells exhibited poor performance due to the oxidation of  $\text{Ge}^{2+}$ .  $\text{CsGeX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) QRs (Fig.III.4c) were prepared by a solvothermal method. The emission wavelength could be tuned from 607 to 696 nm by changing the composition of the different halides (Fig.III.4d) PCE of 4.94% for solar cells based on  $\text{CsGeX}_3$  could be achieved with  $V_{\text{oc}} = 0.51 \text{ V}$ ,  $\text{FF} = 0.51$ , and  $J_{\text{sc}} = 18.78 \text{ mA cm}^{-2}$ . The EQE values of the top-performing devices were observed to exceed 66% (for  $\text{CsGeCl}_3$ ), 68% (for  $\text{CsGeBr}_3$ ), and 79% (for  $\text{CsGeI}_3$ )



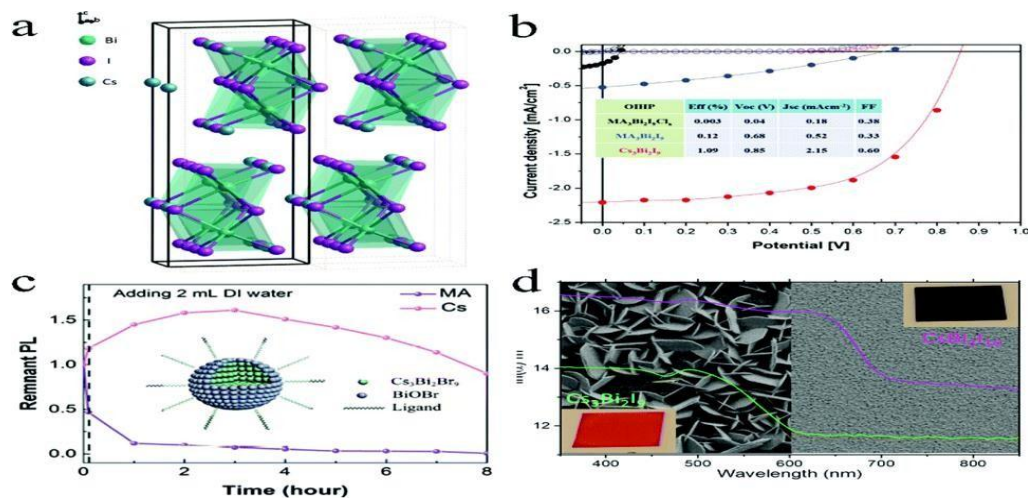


**Figure III.4:**(a) Band structure of CsGeI<sub>3</sub>, MAGeI<sub>3</sub>, and FAGEI<sub>3</sub>. (b) Crystal structure of CsGeI<sub>3</sub>.(c) Morphologies of CsGeX<sub>3</sub> (X = Cl, Br, I) QRs and (d) absorption spectra of CsGeX<sub>3</sub> (X = Cl, Br, I).

### III .6 Using of bismuth in perovskite

Bi is considered as a potential substitute because its valence electronic shell is isoelectronic to Pb. Furthermore, its ionic radius (1.03 Å) is similar to that of Pb (1.19 Å). Therefore, Bi has attracted considerable attention for use in halide perovskite optical applications. In the structure of A<sub>3</sub>Bi<sub>2</sub>X<sub>9</sub>, A and X atoms are the closest-packed and Bi atoms occupy two-thirds of the octahedral X<sub>6</sub> voids. Park *et al.* prepared Bi-based perovskites with the chemical structure A<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> (A = MA<sup>+</sup>, Cs<sup>+</sup>), which consisted of (Bi<sub>2</sub>I<sub>9</sub>)<sub>3</sub> clusters surrounded by cations (Figure.III.5).Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> exhibited five times higher PL intensity when compared with the other two perovskites (MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>Cl<sub>x</sub> and MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>). Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>-based devices exhibited the best performance with  $J_{sc} = 2.15 \text{ mA cm}^{-1}$ ,  $V_{oc} = 0.85 \text{ V}$ ,  $FF = 0.60$ , and  $PCE = 1.09\%$  (Figure.III.5).Furthermore, the light absorption spectra and PCE showed marginal changes after one-month storage (in dry air, humidity less than 10%, and in the dark). It has been demonstrated that Bi-based perovskites exhibited high PLQY and stability against moisture and heat. Such enhanced stabilities could be attributed to their lower-dimensional crystal phase as compared to regular 3D Pb halide perovskites, but the lower dimension also accounts for the lower PV performance. Cs<sub>3</sub>Bi<sub>2</sub>X<sub>9</sub> NCs were synthesized by a facile room-temperature reaction. The emission wavelength could be tuned from 400 nm to 560 nm with different halide compositions. The PLQY of Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>3</sub> was improved from 0.2% to 4.5% by adding oleic acid surfactant that passivated the fast trapping process. Furthermore, Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> NCs exhibited high air stability for

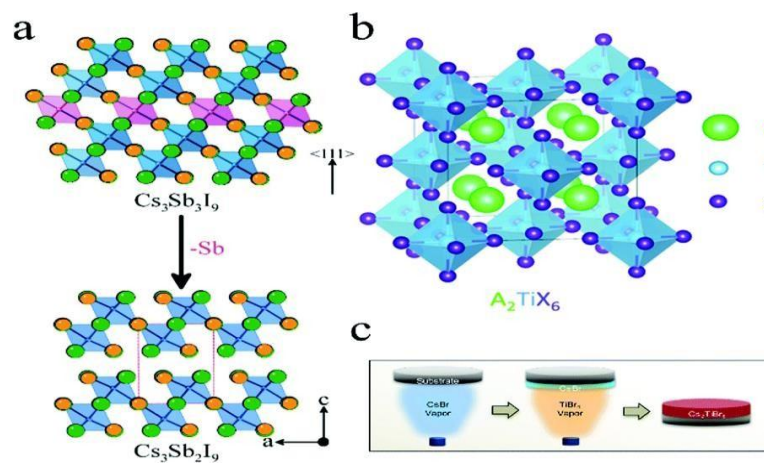
over 30 days because the adsorption of water on the surface of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  formed perovskite hydrates, thereby passivating the perovskite.



**Figure III. 5:**(a) Crystal structure of  $\text{Cs}_3\text{Bi}_2\text{I}_9$  and (b) performance of solar cells fabricated using Bi-based perovskites. (c) Stability of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  against moisture.(d) Quality of  $\text{Cs}_3\text{Bi}_2\text{I}_9$  and  $\text{CsBi}_3\text{I}_{10}$  films.

### III.7 Using of antimony in perovskite

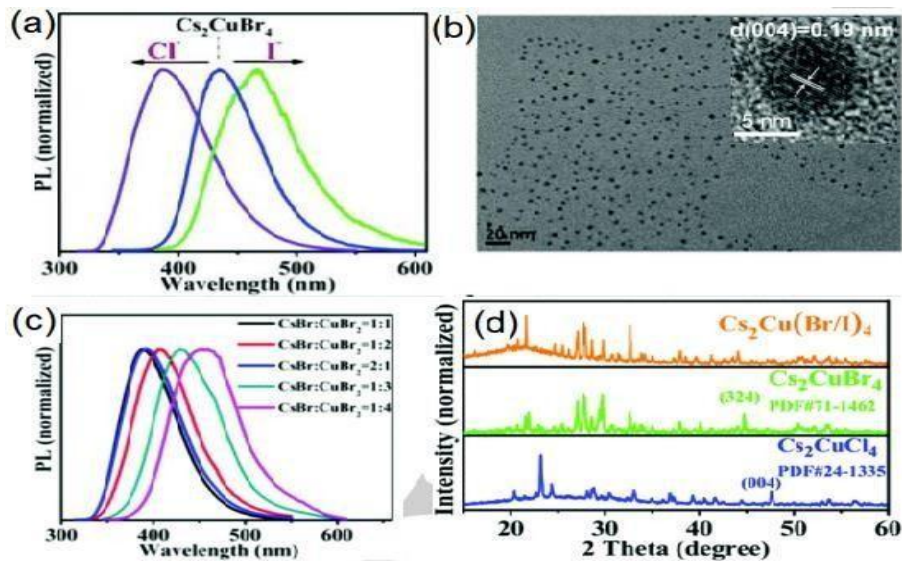
The structure of  $\text{A}_3\text{Sb}_2\text{X}_9$  is the same as  $\text{A}_3\text{Bi}_2\text{X}_9$ , where  $\text{Cs}_3\text{Sb}_2\text{I}_9$  also possessed the 0D dimer form and 2D layered form. 6a shows the 2D structure of  $\text{Cs}_3\text{Sb}_2\text{I}_9$ .  $\text{Cs}_3\text{Sb}_2\text{I}_9$  exhibited indirect band gap of 2.05 eV and enhanced stability against ambient conditions as compared to those of  $\text{MAPbI}_3$ . However, the solar cells based on  $\text{Cs}_3\text{Sb}_2\text{I}_9$  exhibited a  $V_{oc}$  value of 0.25–0.30 eV, which is lower than its organic–inorganic hybrid analogue  $3\text{Sb}_2\text{I}_9$ .



**Figure.III.6.**(a) Structures of  $\text{Cs}_3\text{Sb}_3\text{I}_9$  and  $\text{Cs}_3\text{Sb}_2\text{I}_9$ . (b) Structure of  $\text{A}_2\text{TiX}_6$  (c) Schematic illustration for preparing  $\text{Cs}_2\text{TiBr}_6$  by vapor deposition method.

### III .8 Using of copper in perovskite

Copper-based hybrid organic-inorganic and all-inorganic perovskite might be a promising candidate as non-lead perovskite for reduced toxicity of Cu. The Cu-based halide perovskites crystallize in  $A_2MX_4$  structure. Yang et al reported very recently for the first time synthesis of all inorganic  $Cs_2CuX_4$  QDs by LARP technique at room temperature (Figure.III.7). The bromide and chloride perovskite crystallized in the orthorhombic phase. Pure  $Cs_2CuCl_4$ ,  $Cs_2CuBr_4$  and  $Cs_2CuI_4$  QDs showed strong emission at 385, 410 and 504 nm respectively. The PL emission of  $Cs_2CuBr_4$  was finely tuned from 388 nm to 466 nm by varying precursor ratio  $CsBr:CuBr_2=1:1$  to  $1:4$  (Figure.III.7). The absolute PLQY of  $Cs_2CuBr_4$  QD was reported to be in the range of 32.8% to 37.5%. The value is quite promising for application in LED and electroluminescence. Whereas the PLQY for  $Cs_2CuCl_4$  has been achieved as high as 51.8% which is much more than that  $CsPbCl_3$  system (Figure.III.7). The QDs has been reported to be highly stable in ambient condition. The intensity of  $Cs_2CuBr_4$  only decreased to 92% of the initial value after aging for 30 days, implying a good robust optical stability for optoelectronic applications. [9]



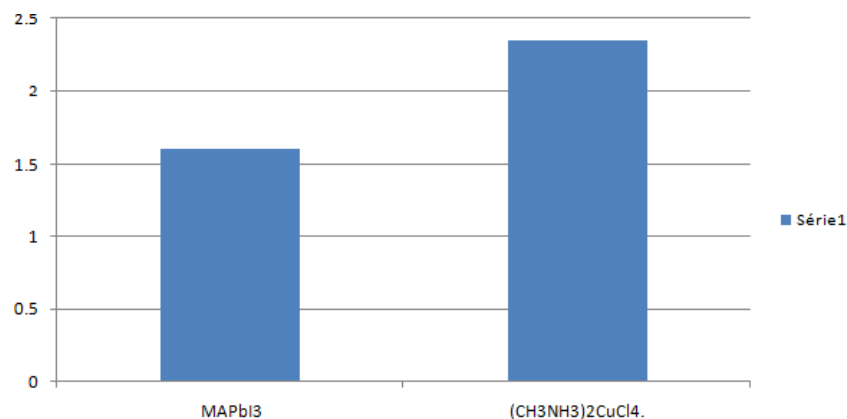
**Figure.III.7.**Fast anion exchange of  $Cs_2CuBr_4$  QDs. (a) PL spectra of mixed halide  $Cs_2CuX_4$  ( $X=Cl$ , Br and their mixture) QDs obtained via anion-exchange reactions(b) TEM and HRTEM image of  $Cs_2CuX_4$  NCs.(c) PL of  $Cs_2CuBr_4$  QDs by with different ratio of CsBr and CuBr<sub>2</sub>. (d) XRD patterns of  $Cs_2CuCl_4$ ,  $Cs_2CuBr_4$ , and  $Cs_2Cu(Br/I)_4$  QDs. Pannel (a-d) are adapted from ref.

### III.9 Comparison between Pb and Cu in optoelectronic properties

Here we made a comparison in optoelectronic properties such as PCE, Voc, Jsc, F, and band gap between the famous lead halide perovskite it is  $\text{MAPbX}_3$  (MA: methyl-ammonium  $\text{CH}_3^- \text{NH}_3^+$ , X=halogen), the triiodide specimen ( $\text{MAPbI}_3$ ) is still the material of choice for solar energy applications and the green copper (Cu)-based hybrid perovskite materials with formula of  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$ .

#### III.9.1 Band gap

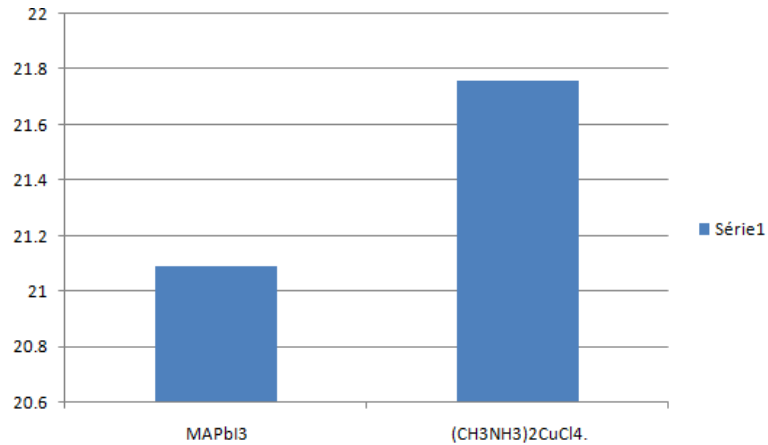
The band gap is the basic characteristic of a light harvester which controls the maximum theoretical power conversion efficiency. It is recognized to possess direct control by way of the actual performance of the perovskite cell device. The wider band gap is particularly important for allowing devices that use them to operate at much higher temperatures, on the order of 300 °C. This makes them highly attractive for military applications, where they have seen a fair amount of use. In figure III.8 we see that the Cu has wider band gap than Pb.



**Figure III.8.** Band gap comparison between  $\text{MAPb}_3$  and  $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$  [10],[11].

#### III.9.2 Power conversion efficiency

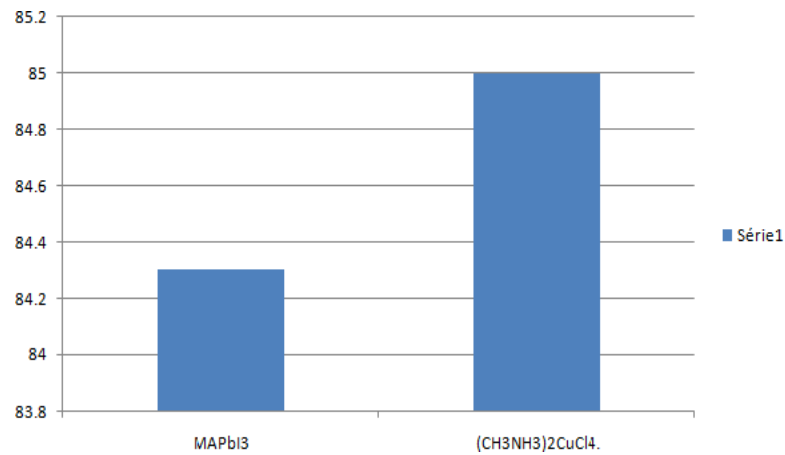
The conversion efficiency is a measure of the performance of a solar cell which could be determined by the maximum output power of the device as the ratio of power output to power input where the input power is the sum over all wavelengths which is commonly fixed at 100mW/cm, We notice in Figure III.9 that the Cu has bigger power conversion efficiency than Pb.



**Figure III.9** .PCE comparison between MAPb<sub>3</sub> and (CH<sub>3</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub> [11],[12].

### III .9.3 Fill factor

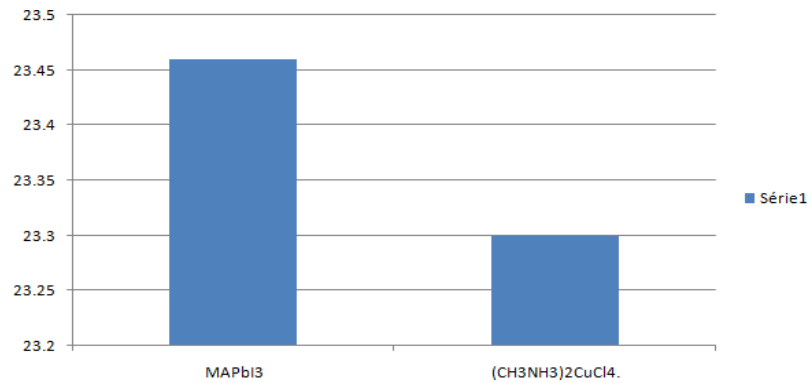
The Fill Factor (FF) is essentially a measure of quality of the solar cell. It is calculated by comparing the maximum power to the theoretical power that would be output at both the open circuit voltage and short circuit current together , the figure III.10 shows that the Cu has higher fill factor than Pb



**Figure III.10** .FF comparison between MAPb<sub>3</sub> and (CH<sub>3</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub> [11],[12].

### III .9.4 Current density J<sub>sc</sub>

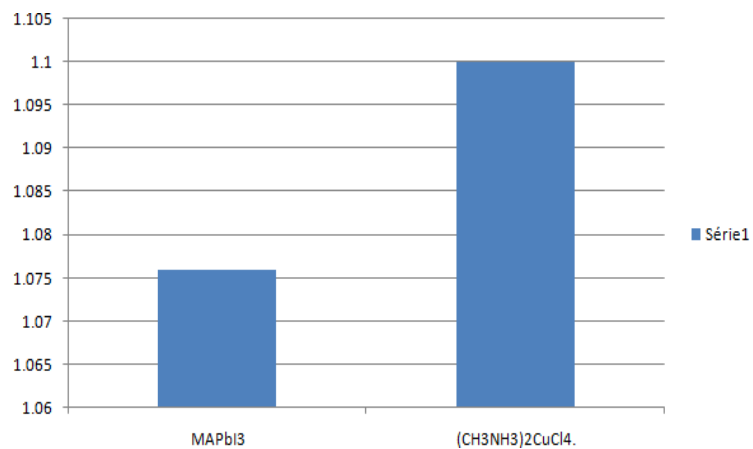
The short-circuit current density J<sub>SC</sub> is the current density at zero voltage (mA/cm<sup>2</sup>), Here the current density of Cu is almost similar than Pb



**FigureIII.11.** Jsc comparison between MAPb<sub>3</sub> and (CH<sub>3</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub>[11],[12].

### III .9.5 Open circuit voltage Voc

The open-circuit voltage,  $V_{OC}$ , is the maximum voltage available from a solar cell, and this occurs at zero current. The open-circuit voltage corresponds to the amount of forward bias on the solar cell due to the bias of the solar cell junction with the light-generated current. we can see in FigureIII.12 That Cu bigger than Pb.



**FigureIII.12.** Voc comparison between MAPb<sub>3</sub> and (CH<sub>3</sub>NH<sub>3</sub>)<sub>2</sub>CuCl<sub>4</sub> [11],[12].

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# General Conclusion

## General conclusion

The purpose of this thesis is to study the solar cell a theoretical study starting from the date of its appearance BC to the present, and generalities about its characteristics, such as its working principle, and the different generations that passed through it. From the first generation that relied on silicon, then the second generation of thin films, and then the third generation that contains types such as organic cells. And finally, the fourth generation, which depends on polymers. We have also given a definition of perovskite, a material with the same composition; Titanium and calcium oxide, and we mentioned the patterns in their shape such as simple perovskite in which A and B are occupied by a unit atom such as  $\text{CaTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{NaTaO}_3$ ,  $\text{PbTiO}_3$  and the complex perovskite in which A and B are occupied by several atoms such as  $(1/2\text{Na}1/2\text{Bi})\text{TiO}_3$ ,  $\text{Pb}(1/3\text{Mg}2/3\text{Nb})\text{O}_3$ ,  $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{1-y}\text{Zr}_y)\text{O}_3$ . We also discussed the synthesis of perovskite materials, considering the synthesis an important factor in the strength of physical, chemical and optical properties. We mentioned the three methods of synthesis, namely, synthesis in the solid state, synthesis in the liquid state and synthesis in the gaseous state we then highlighted metal halide perovskites (MHPs) which are an unconventional family of crystalline materials with continuous expansion of compositional and structural spaces. This material in essence it possesses soft crystal lattices that not only contribute to the extraordinary internal carrier dynamics but also lead to its easy interaction with the external environment (material, light, temperature, electrical field, etc.) and it also contains lead, which is not hidden from us that it is a toxic substance and harmful to human health, and can cause kidney failure and impaired brain development, so we tried to find alternatives that are closer to the efficiency of lead and less toxic at the same time, such as tin, germanium, bismuth and antimony. . But it turns out that they have defects that may affect the performance of solar cells, such as instability, rapid oxidation of these materials, and poor efficiency under high temperatures. So we presented an ideal alternative from our point of view which is copper due to its remarkable properties such as the band gap of 2.36V, the power conversion efficiency 21.76%, filling factor 85%, and open circuit voltage 1.1V. we found in all these properties that copper is more than lead in merit, so we say from our point of view that copper can replace lead if it receives much attention in the future...