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Chap. 22 : Framework structure materials in photovoltaics based on perovskites 3D

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Abstract : The inorganic and hybrid organic / inorganic perovskites based on lead halide and derived materials (alloys) having the formula ABX_3 are emerging as a new and innovative family of absorber materials for the conversion of solar energy into electricity in photovoltaic systems. Thanks to their composition, perovskites and derivatives have exceptional optical, electrical and structural properties with high absorption of light in the visible solar spectrum and good mobility of charge carriers generated by photons facilitating the extraction of electric current. Due to these important properties, perovskite solar cells combine a high efficiency of conversion of light into electricity with great ease of preparation and synthesis at very low costs via simple deposition techniques. In this article we review the structural and optoelectronic properties of perovskites 3D exhibiting photovoltaic properties, we are also interested in the operating principle of perovskite-based solar cells, charge transport materials and associated architectures. Simple fabrication techniques and issues with stability and hysteresis are also discussed.

Keywords : SOLAR CELLS, PEROVSKITES 3D, PEROVSKITE SOLAR CELLS (PSCs), PHOTOVOLTAICS

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I. Introduction

The field of photovoltaics is in constant progress since decades but last years have known an accelerated development. Photovoltaic solar cells, that convert light directly into electricity, are distributed according to 4 generations. The first one comprises cells based on a single p-n junction, typically of silicium. Silicium-based technologies account for most of solar pannels still in use, with monocrystalline, polycrystalline, and amorphous silicon cells with conversion efficiency respectively around 24%, 20%, and 10%, and production costs varying accordingly. Another technology, of hybrid silicon cells was also used, combining different materials (for instance a film of amorphous silicon deposited on top of a monocrystalline layer).

The second generation solar cells is that of thin film technology, mainly of amorphous silicon, CdTe and also copper indium gallium diselenide (CIGS), with the aim of reducing the part of costs depending on the materials. In such technologies the semiconductor material films are indeed only a few micrometers thick, and lower production costs were reached, whereas the conversion efficiency is well comparable to that of more expansive first generation cells. In spite of these advantages, they are still counting for about 17% in solar pannels.

The third generation solar cells has appeared more recently as a result of the quest for lower costs or higher efficiencies; they are not based on the traditional p-n junction. Low costs were obtained with so called Dye Sensitized Solar Cells (DSSCs , named also Grätzel's cells) and organic solar cells, but at the price of a lower efficiency. Cells with improved efficiencies appeared on the other hand as the result of strategies to overcome the thermodynamic limit inherent of technologies based on single p-n junction (so called Shockley-Queisser limit, see next paragraphs). If higher efficiencies were actually reached, this was at the price of higher production costs, the corresponding cells having a more complex structure than traditional ones (multijunction cells, multiband cells, and others allowing to convert a wider range of solar spectrum and consistent with concentrated solar power).

Few years ago, the fourth generation solar cells appeared, with the occurrence of cells developed with the aim of improving charge transport and optical coupling; typically they involve hybrid - inorganic crystals within a polymer matrix.

Perovskites entered photovoltaics with the work of Miyasaka in 2009, who explored the replacement of organic dyes in DSSCs by perovskite light absorbers. The first

specimen of this type of cell presented an efficiency of 3.8% but the big problem was the dissolution of perovskite materials by the liquid electrolyte in short times.

Thereafter considerable progresses were obtained. The aim of this article is to report for non-specialists of photovoltaics, on the most important results and problems of perovskites in solar cells, and to review the various materials of the FWS type which have shown, or could show an interest in photovoltaic cells.

This chapter supposes no knowledge of photovoltaics and introduces basic concepts necessary to understand the presented results. It is organized as follows: the next paragraph is devoted to generalities on photovoltaics and solar radiation, the third paragraph is a general review on perovskites in solar cells presenting the different types of perovskite solar cells, their structure, and their properties. Perspectives and problems are also developed.

II. Basic principles of photovoltaics

II.1 Operating principle of a photovoltaic cell

A photovoltaic cell is a device that converts light into electrical energy. This conversion is only possible in semiconductors when the photons absorbed by the material have an energy equal to or greater than the width of the “forbidden” band between valence band and conduction band, called the gap of the material, generally denoted by E_g . The gap E_g is characteristic of the semiconductor material and strongly depends on the temperature T , and on the manufacturing conditions of the material. There are direct gap semiconductors and indirect gap semiconductors. Properties of semiconductors are presented in several basic textbooks not listed here, to which readers should refer. An electron initially in the valence band, when excited by an incident photon having an energy larger than the bandgap goes to the conduction band and leaves a “hole” in the valence band, seen in electronics as a quasiparticle.

The simplest semiconductor solar cell is a device formed by the junction of two semiconductors of different conduction, one doped type p (the holes are the majority carriers and the electrons the minority carriers) and the other doped type n (the electrons are the majority carriers and the holes the minority carriers). Bringing a p-doped semiconductor into contact with an n-doped semiconductor causes the diffusion of carriers to occur on either side of the junction. Following this phenomenon of

diffusion, the electrons and the holes of the two semiconductors will recombine, leaving in place fixed ions bound to the crystal lattice whose charges are no longer compensated by those of the free carriers. These fixed ions constitute two layers of charges (positive on the n side and negative on the p side) which are the source of an electric field $\mathbf{E}$ in the transition zone called the depletion zone. This field tends to maintain the majority carriers in their respective regions thus opposing their diffusion across the junction. On the other hand, this field favors the passage of minority carriers through the junction.

The photovoltaic effect in semiconductors exploits the presence of the space charge region to collect the carriers (electrons and holes) generated by light, thanks to the electric field that exists in this region. The principle of a photovoltaic cell is therefore to act on the electrons and holes (minority carriers) generated by the light to move each one towards the depletion zone or to generate them in this zone, where they can be collected to produce electricity in an external circuit.

The behavior of these free carriers generated by incident photons differs according to the place of their creation.

- In the electrically neutral regions doped p and n, the minority photocarriers (electrons for region p and holes for region n) diffuse, those which reach the space charge zone are accelerated by the electric field towards the region where they become the majority. These photocarriers therefore contribute to the current through their diffusion, they create a diffusion photocurrent.
- In the space charge zone, the electron-hole pairs created by the photons are dissociated by the electric field, the electron is accelerated towards the region type n and the hole towards the region type p. These carriers give a photocurrent of generation.
- These different contributions add up to create a resulting photocurrent I_{ph} which contributes to the reverse current of the diode.

II.2 Solar spectrum

The main interest of photovoltaic cells is to convert solar energy. The light received from the sun has an emission spectrum comparable to that of a black body estimated at approximately 5800 K, extending over a wide range of wavelengths between Ultraviolet (UV) and Infrared (IR). This radiation is represented by an irradiance spectrum as a function of wavelength. Integrating irradiance over the entire spectrum makes it possible to obtain the power (in W.m^{-2}) supplied by the radiation. However when light rays pass through the Earth's atmosphere, they undergo an attenuation caused by scattering and absorption of certain wavelengths by molecules present in

the atmosphere (O_3 , O_2 , H_2O , CO_2) [1]. Climatic conditions naturally influence these phenomena. The irradiance spectrum in space is therefore different from the spectrum on Earth. The performance of a photovoltaic cell depends on its geographical position. In order to avoid confusion, standardization has been introduced by defining reference solar spectra. The concept of Air-mass (AM) was established in order to be able to compare the different spectra used, this parameter corresponds to the layer of atmosphere crossed by light before reaching the cell. It is defined by :

$$AM = \frac{1}{\cos(\theta)} \quad (1)$$

Where θ is the angle between rays originating from the sun and zenith (Figure 1).

Figure 1. Definition of the AM standard

The solar spectrum in space corresponds to the value air-mass 0 (AM0) and leads to an average illuminance of 1353 W.m^{-2} , while the value 1 (AM1) leads to an average illuminance of 931 W.m^{-2} and corresponds to the solar spectrum received on Earth when the Sun is at the zenith. The AM0 spectrum is used as a reference for solar cells for space use. When the sun makes an angle of 48.2° with respect to the zenith, the air-mass value corresponds to 1.5, the spectrum received on Earth is called AM1.5 and leads to an average illumination 834 W.m^{-2} [2].

The AM1.5G spectrum (G stands for Global) is the most commonly used. This is a distribution of the total solar irradiance including the direct spectrum and the diffuse spectrum.

Figure 2. Standardized spectral irradiance (AM1.5G), adapted from data of [3]

A normalization factor is applied to pass the intensity of the spectrum artificially to 1000 W.m⁻² with an AM1.5 atmosphere crossing. The AM1.5G spectrum is now used as the standard for standardized testing of solar cells for terrestrial applications. The solar spectrum normalized to 1000 W.m⁻² is represented in Figure 2 [2-3].

II.3 Shockley-Queisser theory

The theoretical maximum conversion efficiency of a single junction solar cell as a function of the energy band gap of the material was theoretically approached by William Shockley and Hans-Joachim Queisser in 1961. Based on this theory which used a simplified model of the solar spectrum assimilating the sun as a black body with a temperature of 6000 K and the cell at a temperature of 300 K, the results provide for a limit efficiency of ~ 30% corresponding to a gap of 1.1 eV [4]. The most recent calculations based on this same theory place the limit of the conversion around 33.7% corresponding to an optimal gap of the order of 1.34 eV for an incident solar

power of 1000 W.m^{-2} (AM 1.5 G solar spectrum) [5]. This result (33.7% and 1.34 eV) is still called the Shockley-Queisser limit in their honor [6]. This means that the limit electric power that the solar cell based on a single PN junction can provide is 337 W.m^{-2} . This model also provides the maximum open circuit voltage as a function of the gap, as well as the short-circuit current.

The Shockley-Queisser limit only applies to cells having a single p-n junction with no concentration of solar radiation, cells with multiple layers (multilayer or tandem) can exceed this limit.

II.4 Equivalent model of a solar cell

Usually the photodiode model is used to model the operating of a solar cell. The solar cell (in the case of inorganic materials) is a photodiode that operates without external polarization and delivers its photocurrent through a load.

The characteristic equation of the solar cell is given by:

$$I = I_{ph} - I_0 \left(e^{\frac{q(V+R_s I)}{\eta K T}} - 1 \right) - \frac{V+R_s I}{R_{sh}} \quad (2)$$

I_0 is the saturation current of the photodiode, K is the Boltzmann constant, η is the ideality factor, T is the temperature. I_{ph} is the photocurrent generated by the illumination, R_s is the series resistance, R_{sh} is the shunt resistance, V is the bias voltage that appears across the load connected to the solar cell. I is the current supplied by the photodiode. The associated equivalent electrical diagram is shown in Figure 3 and the current-voltage characteristic curve in Figure 4.

Figure 3. Equivalent electrical diagram of solar cell

Figure 4. Current-voltage I-V (red curve) and power (blue curve) characteristics

I_{sc} : short-circuit current (A)	$FF = \frac{I_m \times V_m}{I_{sc} \times V_{oc}}$
V_{oc} : open-circuit voltage (V)	FF : Fill factor
P_m : maximum power (W)	$efficiency = \frac{P_m}{P_{solar}} = \frac{P_m}{S_r \times A_s}$
$P_m = I_m \times V_m$	S_r : Solar radiation ($W.m^{-2}$)
(I_m, V_m) : maximum power point	$S_r = 1000 W.m^{-2}$ under standard conditions
P_{solar} : Incident solar power (W)	A_s : Active surface of solar panels (m^2)

- The short-circuit current I_{sc} corresponds to the current obtained when the bias voltage V is zero. This is the most important current that can be obtained with a solar cell. It is measured by connecting an ammeter directly to the terminals of the solar cell.
- The open-circuit voltage V_{oc} is the voltage that must be applied to the solar cell to cancel out the current generated by light. It is obtained when the current flowing through the cell is zero. It is measured by connecting a voltmeter directly to the terminals of the solar cell.
- The series resistance R_s is related to the bulk resistivity and impedance of electrodes and materials. The slope of the curve $I(V)$ at the point V_{oc} represents the inverse of the series resistance ($1/R_s$). The shunt resistance R_{sh} is linked to the contact effects and to the bulk recombinations, it models the leakage current. The slope of the curve $I(V)$ at point I_{sc} represents the inverse of the shunt resistance ($1/R_{sh}$). To minimize losses it is necessary to decrease R_s and increase R_{sh} . The ideal case is represented by R_{sh} equal

to infinity and R_s equal to zero.

- The fill factor FF is an indicator of the quality of the solar cell and provides information on its state of aging. It results from series and parallel resistances. It is between 0 and 1.
- The photovoltaic conversion efficiency of the solar cells is defined as the ratio between the maximum power delivered by the cell P_m and the incident light power P_{solar} .

II.5 Technologies, materials, and performances

There are two basic approaches in the technology of making solar cells :

The first is to make the p-n cell with a high quality mono-crystalline or multi-crystalline crystal plate (wafer), its goal is generally high efficiency. This technology is dominated by silicon and III-V compounds such as GaAs and InP. Their yield is in order of 20% to 26% for the single crystal and of the order of 15% to 20% for the multi-crystal.

The second approach consists in making the cells in thin layers, deposited on an inexpensive substrate such as glass, plastic or metal foil. There are several involved compounds as amorphous silicon (a-Si), also III-V compounds, II-VI compounds Cadmium telluride / Cadmium sulfide (CdTe / CdS), or chalcopyrite based on Cu-III-VI₂ (Copper indium diselenide CuInSe₂ : CIS, and Copper indium gallium diselenide CuIn_xGa_{1-x}Se₂ : CIGS), the kesterite CZTS (copper zinc tin sulfide Cu₂ZnSnS₄ : I₂-II-IV-VI₄), the organic solar cells, the dye-sensitized solar cells (DSSCs) and some perovskite solar cells (PSCs). The yields of thin film solar cells vary between 1% and 23% depending on the technology.

The different photovoltaic technologies are currently classified into three generations (or even four generations), we distinguish the first generation, second generation and third generation solar cells. In Figures 5-a, 5-b, 5-c and 5-d, we show examples of architecture of solar cells of the first (Figure 5-a) , second (Figure 5-b) and third generation (Figures 5-c and 5-d).

In the third generation solar cell, we have:

- **Organic photovoltaic cells (OPV)** in which light is absorbed by organic materials (carbon-based). The donor or acceptor nature of organic materials (Figure 5-c) is generally not determined with respect to a dopant but in relation with the electronegativity scale of the materials considered. Organic cells are classified into several types: monolayer cells (this type of cell uses an organic semiconductor of the donor or acceptor type), cells with a donor / acceptor heterojunction (planar, bulk : interpenetrating system, interdigital system). The principle of extracting charges in inorganic materials previously studied differs from the principle of collecting charges in

Figure 5. Structure of the solar cell: (a) silicon (mono or multi-crystalline), (b) thin film solar cell (CIS, CIGS, CZTS) : ZnO / CdS / (CIS, CIGS, CZTS), (c) planar heterojunction bilayer organic solar cell, (d) Dye-sensitized solar cell (DSSC)

organic materials. The working principle of an organic cell can be divided into four parts : light absorption and exciton¹ generation, exciton diffusion, exciton dissociation

¹ An exciton is created when a semiconductor absorbs a photon of higher energy than its bandgap. The excited electron leaves the valence band where a hole is created, and goes to the conduction band. The exciton is the state of the electron

at the donor/acceptor interface and charge generation, transport and collection of charges to the contact electrodes. The best yield obtained is around 12%.

- **Grätzel cells** or hybrid cells sensitized by a Dye (DSSCs, Dye Sensitized Solar Cells) are photoelectrochemical cells and function differently from that of inorganic or organic cells described above. In a Grätzel cell, the part that absorbs light is an organic or metallo-organic dye called sensitizer (S), grafted at the surface of an inorganic n-type semiconductor oxide (TiO_2 , ZnO , SnO_2 , Nb_2O_5).

Usually, a layer of titanium dioxide TiO_2 , nanocrystalline having a nanoporous structure with a large specific surface area for the adsorption of the dye is used. The dye is in direct contact with a liquid electrolyte containing a redox couple, generally triiodide / iodide : called mediator. The assembly is between two conductive electrodes deposited on substrates often made of glass. During the absorption of a photon, the sensitizer changes from its fundamental state to the excited state ($S_0 \rightarrow S^*$), and it injects an electron into the conduction band of the n-type semiconductor (TiO_2) on which it is grafted (S^+ form) (see Figure 5-d). The injected electron passes through the semiconductor layer to reach the external circuit via the transparent conducting oxide electrode (TCO), which generates the current. These cells reached around 11% maximum efficiency.

The first Perovskite solar cells (PSCs) appeared in the frame of DSSCs with the idea to search for various alternative sensitizers. The first prototype of PSCs was thus produced with the structure of a liquid DSSC in 2009 by T. Miyasaka et al. by replacing the classic organic dye usually used as absorber with an absorber based on organic-inorganic hybrid perovskite, lead methylammonium iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) on the one hand and lead methylammonium bromide $\text{CH}_3\text{NH}_3\text{PbBr}_3$ on the other hand (MAPbBr_3). These hybrid perovskites absorb light strongly and widely in the visible range, so that a full light absorption can be achieved in films even as thin as 500 nm. These solar cells offer good yields and various configurations as shown in the next paragraphs.

- **Tandem or multi-junction (MJ)** solar cells include several p-n junctions made of different semiconductor materials. In a tandem device, the cells have different forbidden energy bands arranged in decreasing fashion, allowing a wider absorption of the solar spectrum and limiting energy losses by thermalization. However, efficiency has increased with multi-junction solar cells and this type of structure seems to be the only realistic option to achieve high yields. Currently, tandem cells have optimum yields of around 40%.

and the electron hole bound to each other by the electrostatic Coulomb force.

III. Perovskite materials for photovoltaics

In the last decade, many compounds of perovskite family were investigated in view of applications in photovoltaics; we review main results obtained on the materials themselves in the present part. Their integration in a complete cell is presented in part IV.

Hybrid lead halide perovskites (organic-inorganic) MAPbI_3 and MAPbBr_3 revealed their great interest in several photovoltaic architectures and have shown very impressive photoconductive properties, thus exposing their qualities as intrinsic ambipolar semiconductors. These materials are presented in details in chapter 4 of the present volume. This new photovoltaic technology seems to be a point of convergence between the inorganic and organic solar cells, combining some of their characteristics and properties. In addition to their excellent photoelectric properties, this new emerging solar cell technology also combines low manufacturing cost, easy deposition and high efficiency (10% –21%).

The first observation of the photoconductive properties of perovskites with halides ($X = \text{Cl}, \text{Br}$ or I) was carried out in 1959 by Møller, who showed that lead compounds based on cesium CsPbX_3 could behave like semiconductors [8]. In 1978, the German crystallographer Dieter Weber had the idea to replace the cation A by an organic molecule within the perovskite structure and was able to synthesize for the first time organic-inorganic hybrid perovskites $\text{CH}_3\text{NH}_3\text{BX}_3$ ($A = \text{CH}_3\text{NH}_3^+$, $B = \text{Pb}^{2+}$, Sn^{2+} and $X = \text{I}^-, \text{Cl}^-$ or Br^-) and reported the absorption properties of these compounds [9]. The use of these hybrid methyl ammonium halide perovskites as photovoltaic materials did not emerge until 2009, when Miyasaka et al. replaced the absorbent layer in the dye-sensitized solar cell (DSSC) by lead methylammonium iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) showing a surprising efficiency of about 3.8% and thus achieving the first functional hybrid perovskite solar cell [10]. Since then, a variety of cells based on hybrid perovskites have emerged. The exceptional rise in performance based on these materials gives them a strategic position in solar cell technology. Their efficiency exceeds 20% today.

As seen in other chapters of the present book, several conditions are necessary for the ABX_3 perovskite compounds to form a stable 3D structure :

- Electroneutrality between the charges must be verified, example : $\text{A}^{1+}\text{B}^{2+}\text{X}_3^{1-}$, $\text{A}^{3+}\text{B}^{3+}\text{X}_3^{2-}$, $\text{A}^{2+}\text{B}^{4+}\text{X}_3^{2-}$, $\text{A}^{1+}\text{B}^{5+}\text{X}_3^{2-}$ [11].
- The octahedra BX_6 must be stable [11]. An octahedral factor is defined by [12] :

$$\mu = \frac{R_B}{R_X} \quad (3)$$

For $0.442 < \mu < 0.895$ the coordination is octahedral (the octahedron is stable) [13].

- The size of the ions should meet a certain requirement, it generally imposes the symmetry of the structure and its stability [14]. The tolerance factor t , or Goldschmidt factor, is defined by the following relation [15] :

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \quad (4)$$

(R_A , R_B , R_X are the effective ionic radii for the A, B and X ions, respectively) and for an ideal cubic perovskite structure with a perfectly stacked, stable 3D lattice, the tolerance factor is equal to 1 ($t = 1$). If t is close 1, distortions of the structure occur to stabilize [16] and generally for $0.9 < t < 1$ we have a cubic or pseudo-cubic structure [16, 11]. However outside this interval, for $0.7 < t < 0.9$ the cation A is too small or cation B is too large to form a cubic structure.

Figure 6. Evolution of the Goldschmidt tolerance factor t for a perovskite of general formula $APbI_3$ as a function of the cation A, adapted from data of [33, 34]

The ABX_3 compounds then adopt less symmetrical alternative structures such as the tetragonal, orthorhombic or rhombohedral elementary lattice structure always giving rise to a 3D lattice [11, 16 – 17]. If t is larger than 1 ($t > 1$), the cation A is too large and it may no longer fit into the interstices of the BX_6 octahedra formed by the lattice. In this case, the result is that the 3D lattice arrangement becomes unstable [16, 18 – 20] and the perovskite then adopts, by reorganizing itself, a two-dimensional (2D) lattice structure (instead of 3D) of general formula $A_nB_nX_{3n+2}$ or $A_{n+1}B_nX_{3n+1}$ or apparent structures with various stoichiometries such as the phases Ruddlesden-Popper

$A'_2(A_{n-1}B_nX_{3n+2})$, Aurivillius $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ or Dion-Jacobson $A'(A_{n-1}B_nX_{3n+1})$ [21 – 23]. In Figure 6, we show the evolution of the tolerance factor for perovskite structure $APbI_3$ [33, 34].

III.1 Absorbers based on 3D perovskites

By choosing suitable compounds A, B and X, it is possible to manufacture materials which have the ability to convert light into electricity i.e. absorbers based on perovskites. The choice of these materials and their combinations are crucial to determine the optical, electronic and structural properties of perovskite (band gap and absorption spectra, mobility, diffusion length, crystallinity, etc., see next chapter of the present volume) [14]. Photovoltaic absorber materials based on 3D perovskites having good photovoltaic properties known to date are generally based on lead halide (or tin) $APbX_3$ ($X = I, Cl, Br$) and their alloys, A is a organic monovalent cation (in the case of hybrid perovskites) or inorganic. The cation A often defines the model of the structure; its shape, size and charge distribution are crucial factors in stabilizing the structure of this type of perovskite ($APbX_3$) and it largely influences its optoelectronic properties [24].

III.2 Organic / inorganic hybrid perovskites for solar cells

Empirically, 3D halogenated perovskites (I, Br and Cl) are formed if the octahedral factor μ is between 0.442 and 0.895 and the tolerance factor t is between 0.813 and 1.107 [25]. 3D lead halide organic-inorganic hybrid perovskites have given satisfactory results in photovoltaic applications and have appeared successfully by replacing cation A with a monovalent organic cation. Organic cations such as methylammonium $CH_3NH_3^+$ (MA^+), and formamidinium $CH_5N_2^+$ (FA^+) have been successfully incorporated into the A site of the unit cell and have shown potential to stabilize the 3D perovskite structure [26, 27 – 29]. Their ionic radius also induces a tolerance factor t favorable to a stable 3D structure. The incorporation of these ions has led to excellent photovoltaic properties.

Formamidinium is a slightly higher cation compared to methylammonium, these two cations are small enough to form the 3D perovskite, while ethylammonium is a too large cation [14, 30]. It can be noted more generally that MA^+ belongs to the family of alkylammonium of formula RNH_3^+ and one could think of substituting the methyl group ($R = CH_3$) for other alkyl groups. However, an alkyl radical containing more than two C-C bonds (more than two carbon atoms) gives rise to an organic cation A ($C_nH_{2n+1}-NH_3^+$ with $n > 2$) that can induce a tolerance factor $t > 1$ so that it is no longer possible to

obtain a three-dimensional structure. On the other hand, it is possible to obtain with these groups molecular compounds which reorganize themselves into a two-dimensional structure by adjusting on the stoichiometry, giving rise to the 2D perovskite family of chemical formula $(R-NH_3)_2PbX_4$ [31, 32].

In addition to $MAPbX_3$ or $FAPbX_3$ compounds with $X = Cl, Br$ or I known as 3D organic-inorganic hybrid perovskites which exhibit the best photovoltaic properties, the substitution of lead (Pb^{2+}) by an atom M of the same degree of oxidation (M^{2+}) can lead to alternative materials that could expand the family of these 3D absorbers. These materials must meet a number of criteria such as high light absorption and defect tolerance, good stability, good photovoltaic efficiency to compete with the performance of lead halide perovskites. Among the possibilities for substituting lead, the choice of non-toxic elements which leads to compounds with good photoconductive properties would be a major advance with perovskites. However, there is a wide range of elements with an oxidation degree +2 (divalent) in a stable or unstable state that can substitute for lead and obtaining 3D perovskite AMX_3 will depend on the tolerance factor t and the octahedral factor.

Among the elements capable of replacing lead (Pb^{2+}), one can mention the elements of group 14 such as Ge^{2+} , Sn^{2+} , alkaline earth metals such as Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , transition metals such as Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Pd^{2+} , Pt^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} (toxic), Hg^{2+} (toxic), and lanthanides such as Eu^{2+} , Tm^{2+} , Yb^{2+} . The multiplicity of the oxidation number of an element (example : Sn^{2+} and Sn^{4+} , Fe^{2+} and Fe^{3+}) can however cause stability problems in materials.

The most obvious choice among all these elements is the substitution of Pb by Sn or Ge as these three elements have a similar electronic structure (belong to the same column of the Mendeleïev table). The 3D halogenated hybrid perovskites based on tin $ASnX_3$ ($X = Cl, Br, I$) give to date the best results in photovoltaic applications by replacing lead by a divalent metal M (+2). However, their performance is inferior to that of lead halides and are also less stable. Organic cations such as methylammonium (MA^+) and formamidinium (FA^+) have also been successfully inserted into site A giving rise to the family of 3D absorbers of the types $MASnX_3$ and $FASnX_3$ ($X = Cl, Br, I$).

However, among all these possibilities of substituting lead which is a toxic element, the best results obtained in photovoltaic applications to date are based on lead showing the preponderant influence of this element (despite its toxicity) in the absorbent and photoconductive properties of perovskite materials.

III.2.a Inorganic perovskites for solar cells

Although inorganic perovskites have been somewhat overshadowed by the success of organic-inorganic hybrid perovskites, it is relevant to mention their main properties related to photovoltaics. The first perovskite with reported photoconductive properties was with the cesium-based lead halides CsPbX_3 . The cation A corresponding to Cs^+ . Cesium has a small size (smaller than MA^+ and FA^+) [14], which allows it to fit into the octahedral PbX_6 sites and checks the tolerance factor, thus giving 3D perovskites. The substitution of cesium by elements of the same column of the same degree of oxidation such as Li^+ , Na^+ , K^+ , Rb^+ does not lead to 3D structures (Figure 6) but to 1D perovskites [33] and none photovoltaic property has not been reported with these materials till now. So far, CsPbX_3 is the 3D inorganic lead halide perovskite with the best photovoltaic efficiencies, however some mixed inorganic perovskites could reveal an interest in photovoltaics in future (see next chapter of present volume).

III.2.b Mixed hybrid perovskites for solar cells

So-called mixed perovskites are obtained as the result of occupation of site A or B by several cations and occupation of site X by several anions. The variation in the composition of the APbX_3 perovskite also makes it possible to vary the optoelectronic and structural properties of the material as well as its stability. It is therefore sufficient to develop alloys by partially substituting the cation A (MA^+ , FA^+ , Cs^+), the cation B (Pb^{2+} , Sn^{2+}) and the anion X (I^- , Cl^- , Br^-) in the 3D ABX_3 perovskite to improve photovoltaic performance and long-term stability. In general, the growth of these alloys leads to compounds of the type $(\text{MA})_x(\text{FA})_y(\text{Cs})_z(\text{Pb})_t(\text{Sn})_{1-t}[(\text{I})_x'(\text{Br})_y'(\text{Cl})_z']_3$, such that $x+y+z = 1$ and $x'+y'+z' = 1$.

Obtaining 3D perovskite depends on the composition and proportions of the mixture and is determined from the effective radii of the cations $\text{A} = (\text{MA})_x(\text{FA})_y(\text{Cs})_z$, $\text{B} = (\text{Pb})_t(\text{Sn})_{1-t}$ and the anion $\text{X} = (\text{I})_x'(\text{Br})_y'(\text{Cl})_z'$. In general, the proportions must be balanced to meet the conditions of Goldschmidt. Thus it becomes possible to introduce atoms of small sizes such as Rb^+ or large size such as $5\text{-AVA} = \text{COOH}(\text{CH}_2)_4\text{NH}_3^+$ in balanced proportions, this mixture leads to effective radii which can fulfill the Goldschmidt tolerance factor. Often large size atoms are combined with small size atoms in balanced proportions to obtain the 3D structure. A large number of mixed perovskites have been successfully synthesized and have shown good performance in photovoltaic applications with improved stability. Figure 7 shows the example of the evolution of the tolerance factor of the alloy $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ a function of the effective radius of the composition $\text{FA}_x\text{Cs}_{1-x}$ which corresponds to cation A. Thus the effective

radius of the cation can be modulated by varying its composition. The $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ perovskite corresponds to replacing methylammonium (MA^+) in MAPbI_3 with formamidinium (FA^+) and cesium (Cs^+).

Figure 7. Evolution of the tolerance factor as a function of the effective radius in the FA and Cs mixture, adapted from data of [35].

III.3 Optical properties of perovskites

The sub-family of hybrid lead halide perovskites 3D gathers interesting optical and electrical properties such as high optical absorption as important as the conventional 1st generation or 2nd generation materials used [11], optical band gap which make it possible to collect a wide wavelength range of sunlight and good transport properties for electrons and holes (diffusion length, mobility) in the context of photovoltaic applications [36].

The APbX_3 hybrid halogenated 3D perovskites are semiconductors whose optical band gap is often direct² [11] and their absorption coefficient is so high that a layer as thin as some hundred nm (around 300 nm), has the same absorption than a 300 μm thick layer of silicon (1st generation). This is also comparable to a 3 μm thick layer of CdTe and CIGS (second generation). Alloys based on lead halide (APbX_3) allow to tune the width of the forbidden band in a wider spectrum range from visible to infrared depending on the nature of the substituent elements.

² This corresponds to the situation depicted in Figure 8: the maximum of valence band and the minimum of conduction band occur at the same momentum (k) value so that an electron can be excited without any k -change

Regarding MAPbI₃, in terms of optical properties in photovoltaic applications, this material has:

- a very high absorption coefficient over the entire visible solar emission spectrum, in the order of 10^4 cm^{-1} - 10^5 cm^{-1}
- a gap located around 1.6 eV [37 - 38] which makes it possible to collect a wide wavelength range of sunlight that extends from near infrared to ultra-violet
- good transport properties for electrons and holes [32].

Several models of theoretical calculations to establish the band structure of MAPbI₃ have been developed [39 – 42]; even if the found values of the energy band gap differ according to the model, these calculations generally lead to a structure of bands with a direct gap and some result in values close to the experimental gap as shown in the example of Figure 8. This Figure represents the energy bands versus the wave vector **k**. The points X, R, M, R, Γ are points of the wave vector **k** in the Brillouin zone (BZ) (see Figure 10 of chapter 1, p19 of the present volume, Γ is the center of BZ, and X the center of faces). The band structure shows a direct gap (in the order of 1.6 eV) at point R.

Figure 8. MAPbI₃ band structure calculated by DFT in the tetragonal phase, adapted from data of [43]

However, the use of inorganic semiconductor calculation methods (Bloch functions approach of the periodic structure of 3D perovskites) for the study of hybrid perovskite compounds leads, instead of talking about HOMO (Highest Occupied Molecular Orbital) and LUMO (Lower Unoccupied Molecular Orbital), to speak of valence band and conduction band to describe the electronic structure of hybrid perovskites [31, 32, 44].

The values of the exciton binding energy in MAPbI_3 , are in the range of 5 to 50 meV and are much lower than those found in organic materials which are in the order of magnitude of 1 eV; the binding energy of the exciton varies from 50 to 150 meV for MAPbCl_3 and MAPbBr_3 [32]. It decreases when the temperature increases. It is around some meV at ambient temperature in MAPbI_3 and the excitons are of the Wannier-Mott type [11], which partly explains the very good performance of this material in photovoltaic applications. A low exciton binding energy makes it easy to separate the electron-hole pair induced by the absorption of a photon by the material.

Theoretically, the optimal value of the gap is between 1.1 eV and 1.4 eV for a single junction solar cell [45, 46] leading to research of synthesis of perovskites with a smaller gap since the gap of the MAPbI_3 leader compound is around 1.6 eV. Among the possibilities a total or partial substitution of the elements that make up the perovskite. The last leads to the realization of an alloy in the material. The alloys also allow the solar cell architectures to be extended by juxtaposing several layers and various tandem structures.

- Total or partial substitution (alloy) of cation A :

* In the case of FAPbI_3 where the MA^+ cation is replaced by a slightly larger cation, FA^+ , the band gap is lowered and is around 1.47 eV [47], approaching the optimum value of the gap and also allowing to widen the photon absorption range (by shifting more towards the infrared). In the case where the MA^+ cation is replaced by a small cation, Cs^+ , the forbidden band is increased and is located around 1.7 eV. Figure 9 shows corresponding APbI_3 absorption spectra ($A = \text{Cs}, \text{MA}, \text{FA}$).

Figure 9. Absorption spectra of APbI_3 perovskites ($A = \text{Cs}, \text{MA}, \text{FA}$), adapted from data of [31].

The synthesis of mixed perovskites also makes it possible to tune the energy band gap. The results showed that it is possible to obtain 3D perovskites with a view to improving performance and stability, by making binary, ternary or quaternary alloys of the cation A by mixing different cations Rb^+ , Cs^+ , MA^+ and FA^+ generally leading to $APbX_3$ with $A = Rb_xCs_yMA_zFA_t$ where $x+y+z+t=1$.

* Thus the alloy $FA_xMA_{1-x}PbI_3$ makes it possible to decrease the energy band gap which can vary from approximately 1.64 eV to 1.47 eV by partially substituting the cations MA^+ by cations of MA^+ (by increasing x)

* The 3D perovskite alloy $Cs_xMA_{1-x}PbI_3$ where Cs^+ is a cation smaller than MA^+ , allows to increase the energy band gap which can vary from 1.64 eV to 1.73 eV (by increasing x).

* The introduction of Rubidium Rb^+ cations, slightly smaller than Cs^+ cations, in the composition of perovskite has led to the possibility of new combinations of different cations (Rb^+ , Cs^+ , MA^+ and FA^+) expanding the possibility of making alloys and has led to very promising returns.

* Also the synthesis of a 3D perovskite by producing a mixture of 5-aminovaleric acid (5-AVA) and methylammonium MA^+ of $MA_{1-x}(5-AVA)_xPbI_3$ type gave good yields with an improvement in the stability [48].

Note of writing :

$MA_{1-y}FA_yPb_{1-y}Sn_y(I_{1-y}X_y)_3 = (MAPbI_3)_{1-y}(FASnX_3)_y$ with $X = Cl$ or Br

- Total or partial substitution (alloy) of cation B (Pb^{2+} , Sn^{2+}) :

The energy band gap of $MASnI_3$ is approximately 1.21 eV, this material can then absorb a wider range of the solar spectrum compared to $MAPbI_3$. The realization of a $MAPb_{1-x}Sn_xI_3$ type alloy makes it possible to lower the energy band gap, which can vary from 1.64 eV to 1.21 eV. Although with these alloys we can hope to synthesize materials with energy band gaps close to the optimal gap, the yields remain low and the introduction of tin makes the device less stable [49].

- Total or partial substitution (Alloy) of the anion X (I, Br, Cl) :

The experimental value of the optical gap of $MAPbBr_3$ is 2.34 eV and that of $MAPbCl_3$ is 3.1 eV. Thus, the synthesis of alloys type $MAPb(I_{1-x}Br_x)_3$ increases the gap which can vary from 1.6 eV to 2.34 eV, as for $MAPb(I_{1-x}Cl_x)_3$ alloys the gap which can vary from 1.6 eV to 3.1 eV or also $MAPb(Br_{1-x}Cl_x)_3$ where the gap can vary from 2.34 eV to 3.1 eV. The realization of an alloy by substituting iodine for bromine and then for chlorine, consisting in reducing the radius of the halogen, would increase the forbidden band of the material [50]. In the case of the $FAPb(I_{1-x}Br_x)_3$ alloy, we could increase the gap from 1.47 eV to 2.23 eV by increasing the ratio x. Regarding Fluor F which is also a halogen and having the smallest radius, its substitution for iodine in $MAPbI_3$ leads to

a very small tolerance factor and a high degree of constraint. With its introduction, it would also generate a wider optical gap than that of MAPbCl_3 which is not appropriate for photovoltaic applications [32].

III.4 Electrical properties of 3D perovskites

The values of the mobility, the diffusion length and the lifetime of the carriers are very sensitive to the quality of the crystal or of the polycrystalline film. The values reported in the literature are very dependent on the quality of the material and the processing conditions, which indicates that phenomena are influenced by defects; it seems to be important in particular, to study carefully the phenomena that may occur at interfaces, grain boundaries, domain walls, dislocations, and various other defects. MAPbX_3 3D perovskites have good charge transport properties, mobilities of carriers (electrons and holes) are high, they can vary between $2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and $50 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, the diffusion length of the carriers is in the order of 100 nm to $1 \mu\text{m}$ in thin layers [58 – 60]. These properties are very favorable for photovoltaics and are superior to those of organic semiconductors, the carrier diffusion length of which is estimated at a few nm and mobilities between 10^{-2} and $10^{-1} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [31].

Table 1. Efficiency of some 3D perovskite absorbers and alloys

Absorber (3D perovskite)	Efficiency %	Reference
FAPbI_3	14	[51]
$\text{MA}_{0.06}\text{FA}_{0.4}\text{PbI}_3$	15	[52]
$\text{CS}_{0.2}\text{FA}_{0.8}\text{PbI}_3$	17.61	[53]
FASnI_3	5	[54]
$\text{FA}_{0.8}\text{MA}_{0.15}\text{Rb}_{0.5}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$	20	[55]
$\text{MA}_{0.4}\text{FA}_{0.6}\text{Pb}_{0.4}\text{Sn}_{0.6}\text{I}_3 = (\text{MAPbI}_3)_{0.4}(\text{FASnI}_3)_{0.6}$	15	[56]
$\text{MA}_{1-x}(\text{5-AVA})_x\text{PbI}_3$	12.8	[57]

We list in Table 2 some values of mobility and diffusion length found in the literature. MAPbI₃ is a material with an ambipolar character, electrons are transported as well as holes. Consequently, the values of the diffusion length (100 nm to 1 μm) are quite large since its thickness to absorb the solar spectrum is of some hundred nm (of the same order of magnitude). Thus, the trapping or the recombination of charge carriers takes place slowly (in a time in the order of a hundred nanoseconds) despite its high absorption coefficient which explains its low absorption thickness. However, this apparent contradiction of high absorption and long lifetime of charge carriers could be explained by a direct-indirect nature of the forbidden band [61 – 62].

Many perovskite materials were tested in different architectures, but a lot of investigations still remain to be performed. The next part present main architectures of perovskite solar cells.

Table 2. Some values of mobility found in the literature [63]

Crystal	Growth Method	Carrier Mobility (cm ² .V ⁻¹ s ⁻¹)
MAPbI ₃	STL	105 ± 35
MAPbI ₃ (Cl)	STL	167 ± 35
MAPbI ₃	ITC	34
MAPbCl ₃	ITC	179
MAPbBr ₃	ITC	4.36
MA _{0.45} FA _{0.55} PbI ₃	AVC	271 ± 35

IV. Solar cells based on perovskites

IV.1 Architecture of perovskite solar cells

The structure of perovskite solar cells is complex, involving a stacking of thin layers. So far there are two main architectures, that of mesoporous cells having a configuration similar to Grätzel cells and the planar architecture having a configuration similar to organic and inorganic cells. In all cases there appears a difficulty concerning reproducibility of results: two cells that should be in principle identical, may reveal very different properties in practice. The observed extreme sensitivity on fabrication

conditions, including also the exact characteristics of used reactants, the temperature, humidity, thermal history, etc, should lead scientists to give in future more accurate informations and pay attention to details of fabrication processes. This is certainly a necessary condition to reach a better understanding of PSCs. In the following, we cannot develop these too complex aspects.

In mesoporous architecture, we can distinguish cells with or without a hole transport material (HTM).

Figure 10. Perovskite solar cells n-i-p mesoscopic structure, adapted of [64]

The cell with HTM (Figure 10) is made up of several elements including :

- A glass or plastic substrate (flexible polymer : polyethylene naphthalate PEN)
- A transparent collecting electrode realized as a deposited layer of transparent conducting oxide (TCO) (indium oxide doped with tin - ITO (In₂O₃:Sn), or tin oxide doped with fluorine - FTO (SnO₂ : F) deposited on the substrate glass or polymer)

- An electron transport material (ETM or n-type semiconductor) based on n-type semiconductor oxide in the form of a compact thin film (example: TiO_2 , ZnO) deposited on the electrode transparent collector
- A layer of mesoporous oxide (example: TiO_2 , ZnO , Al_2O_3 , ZrO_2) deposited on the compact thin layer
- The APbX_3 perovskite absorber or its alloys (example MAPbI_3 , $\text{MAPbI}_{3-x}\text{Cl}_x$), infiltrated on the mesoporous oxide layer where it will crystallize
- A hole transport material (HTM or p-type semiconductor) in the form of a compact thin layer (example: Spiro-OMeTAD, PTAA) which covers the perovskite and the meso-porous layer
- A metal collecting electrode (example: Au, Ag) deposited on the hole transport material (HTM)

Structure model: OTC / c- (TiO_2 , ZnO) / m- (TiO_2 , ZnO , SnO_2 , Al_2O_3 , ZrO_2) / perovskite / HTM / metal

Example: FTO / Compact TiO_2 (50 to 70 nm) / Mesoporous TiO_2 (150 to 300 nm) / MAPbI_3 (300 nm) / spiro-OMeTAD (150 to 200 nm) / Au (50 to 100 nm)

In the mesoporous architecture without a hole transport layer we have (Figure 11) :

- A transparent collecting electrode: transparent conducting oxide deposited on the glass or polymer substrate
- An electron transport material (ETM) in the form of a compact thin film (TiO_2 or ZnO) deposited on the transparent collecting electrode
- A layer of mesoporous oxide (TiO_2 , ZnO_2 , Al_2O_3 , ZrO_2) deposited on the thin n-type compact layer
- The APbX_3 perovskite absorber or its alloys (example MAPbI_3 , $\text{MAPbI}_{3-x}\text{Cl}_x$), infiltrated on the mesoporous oxide layer where it will crystallize
- A collecting electrode (example: Au, Ag, carbon)

Structure model: TCO / c- (TiO_2 , ZnO) / m- (TiO_2 , ZnO , SnO_2 , Al_2O_3 , ZrO_2) / perovskite / metal, carbon

Example: FTO / Compact TiO_2 / Mesoporous TiO_2 / MAPbI_3 / Au

The planar architecture does not contain the mesoporous layer, perovskite solar cells are represented by two configurations: the standard n-i-p configuration³ or the inverse

³ n-i-p or p-i-n architectures depend on the stacking of electron and hole transport layers (ETL) and (HTL) relatively to the transparent conductive oxide layer TCO (ITO or FTO).

p-i-n configuration. Indeed, the order n or p refers specifically to the order of deposition of ETL and HTL layers.

Figure 11. (a) Mesoporous architecture of a perovskite-based solar cell without a hole transport material FTO / c-TiO₂ / m-TiO₂ / MAPbI₃ / Au. (b) Energy level diagram showing the process of charge separation, adapted of [65]

The architecture n-i-p includes (Figure 12) :

- A glass or plastic substrate (flexible polymer)
- A transparent collecting electrode of TCO deposited on the glass or polymer substrate
- An electron transport material (ETM) in the form of a compact thin film (TiO₂, ZnO, SnO₂, PCBM) deposited on the transparent collecting electrode
- The APbX₃ perovskite absorber or its alloys (example MAPbI₃, MAPbI_{3-x}Cl_x) in the form of a thin layer
- A hole transport material (HTM) in the form of a compact thin layer (spiro-OMeTAD, PTAA) deposited on the perovskite layer
- A metal collecting electrode (Au, Ag,) deposited on the hole transport material (HTM)

Structure model : glass / TCO / ETL / perovskite / HTL / metal

Example: FTO / TiO₂ compact / MAPbI₃ / spiro-OMeTAD / Au

Figure 12. Perovskite solar cells n-i-p planar structure, adapted of [64]

The architecture p-i-n (or inverted) includes (Figure 13):

- A glass or plastic substrate (flexible polymer)
- A transparent collecting electrode of transparent conducting oxide TCO deposited on the glass or polymer substrate
- A hole transport material (HTM) in the form of a compact thin film (PEDOT: PSS, NiO) deposited on the transparent collecting electrode
- The absorber of perovskite APbX₃ or its alloys (example MAPbI₃, MAPbI_{3-x}Cl_x) in the form of a thin layer
- An electron transport material in the form of a compact thin film (PCBM, C₆₀) deposited on the perovskite
- A metal collecting electrode (Au, Ag) deposited on the electron transport material

Structure model: glass / TCO / HTL / perovskite / ETL / metal

Example : ITO / PEDOT :PSS / MAPbI₃ / PCBM / Ag

In the planar architecture we can also distinguish perovskite solar cells without hole transport material of the type glass / TCO / perovskite / ETL / metal (Figure 14) or perovskite solar cells without electron transport material of the type glass / TCO / HTL / perovskite / metal (Figure 15).

Figure 13. Perovskite solar cells p-i-n planar structure, adapted of [64]

Figure 14. (a) Perovskite solar cell without hole transport material (FTO / TiO₂ compact / MAPbI₃ / Au), (b) energy band diagram showing charge separation, adapted of [66]

Figure 15. (a) Perovskite solar cell without electron transport material (FTO/MAPbI₃/Spiro-OMeTAD/Au), (b) energy band diagram showing charge separation, adapted of [66]

IV.2 Operating principle

Perovskite solar cells generally consist of a stacking of several thin layers depending on their architecture, where the perovskite absorber is sandwiched between an electron transport layer (or electron acceptor material or n-type semiconductor) and an HTL hole transport layer (or electron donor material or p-type semiconductor), all included between two collecting electrodes (the anode which collects the holes and the cathode which collects the electrons; generally one of the electrodes is transparent).

The principle of operation of perovskite solar cells is interpreted differently according to the authors. The diagrams in Figure 16 [67] give an overview on the transfer of charges in a solar cell based on perovskite. After absorption of photons of sufficient energy by the perovskite layer, electron-hole pairs are generated (1), (and if they are weakly bound, they easily dissociate at room temperature). Then, after dissociation of the excitons (and the charge thermalization phenomenon (2)) the electrons are transferred from the perovskite to the ETL layer (3), and the holes in the perovskite layer to the HTL layer (4). However, the mechanism or dynamism of charge transfer (3) and (4) (injection, diffusion or conduction of carriers, separation or dissociation of the exciton) between perovskite and the ETL and HTL layers poses a lot of debate in the literature seeing that perovskite solar cells seem to be a point of convergence with

the different technologies such as Grätzel cells, organic cells and inorganic cells due to its configurations which are similar to those of these different technologies.

Figure 16. Dynamic of charges in the perovskite solar cell : (a) Transfer of charges between perovskite and transport materials (perovskite / ETL and perovskite / HTL) ; (b) Recombination of charges between perovskite and transport materials (perovskite / ETL and perovskite / HTL), and within the perovskite, adapted of [67]

Electrons are carried in the ETL layer (5), and holes in the HTL layer (5), to the contact electrodes where they are collected to deliver electricity. However, this charge transfer phenomenon is also coupled to a mechanism of recombination or carrier losses which can affect the performance of the cell as illustrated in Figure 18-b. These losses can be observed between the perovskite layer and the ETL and HTL transport layers, they can be linked to the presence of recombination centers at the interfaces ((6) and (7)) or to the problems of energy band alignment ((8) and (9)). In perovskite, the losses may be due to the presence of defects or of bulk recombination centers ((10) and (11)), of direct (or radiative) recombination (12), or Auger recombination (13).

It is to note that, in a Grätzel cell, the transfer phenomenon occurs by injection, in an organic cell by assisted diffusion of charge separation at the interfaces, in an inorganic cell by a diffusion and conduction phenomenon whose space charge region allows to recover the generated charges.

IV.3 Transport and contact materials

The choice of ETL and HTL transport materials is constrained by the condition of good alignment of the energy bands, the alignment must be favorable to charge separation and limit parasitical recombination phenomena.

The ETL layer can be composed by the juxtaposition of several electron transport layers and the same for the HTL layer but respecting a certain order of assembly of the layers thanks to the engineering of the bands and the elaboration of the materials. The charge transport layers should have good transport properties with good charge mobility and the contacts at the interfaces should facilitate charge transfer. The discontinuity between the energy bands should not be very elevated (“for example to avoid the spike and cliff effects in the bands in the case of inorganic semiconductors”) for a good transfer of the charges, but also a limitation of the discontinuity of the bands reduces the transparency of the intermediate layers and can thus limit the absorption of the absorbent layer which is not preferable. Therefore one can use ETL or HTL layers largely transparent (high optical gap with low light reflection) while minimizing the discontinuity in the charge transfer bands, i.e. reducing the discontinuity between the conduction band (or LUMO) of ETL and that of the absorber (perovskite), likewise by reducing the discontinuity between the valence band of the absorber (the perovskite) and that (HOMO) of HTL thus by adjusting the position of the materials or also by superimposing several layers having quite close parameters (one can use alloys for example).

In a good alignment in order to avoid problems of back-transfer of charges to the absorbent layer or transfer of charge in a non-transport layer (ETL for holes and HTL for electrons) :

- The valence band (or HOMO) of the ETL layer (E_{VETL} or H_{ETL}) must be less than that of the absorbent layer (or of the perovskite) (E_{VAbs} or H_{Abs}) and the latter must also be less than that of the HTL layer (E_{VHTL} or H_{HTL}). In other words, the valence bands (or HOMO) of the ETL, Absorber (perovskite) and HTL layers must be arranged in an increasing manner respectively.

$$E_{VETL} \text{ (or } H_{ETL}) < E_{VAbs} \text{ (or } H_{Abs}) < E_{VHTL} \text{ (or } H_{HTL})$$

- Likewise the conduction band (or LUMO) of the ETL layer (E_{CETL} or L_{ETL}) must be lower than that of the absorbent layer (or of the perovskite) (E_{CAbs} or L_{Abs}) and the latter must be lower than that of the HTL layer (E_{CHTL} or L_{HTL}). In other words, the conduction bands (or LUMO) of the ETL, Absorber (perovskite) and HTL layers must be arranged in an increasing manner respectively.

$$E_{CETL} \text{ (or } L_{ETL}) < E_{CAbs} \text{ (or } L_{Abs}) < E_{CHTL} \text{ (or } L_{HTL})$$

The diagram in Figure 17 illustrates the arrangement of materials in a photovoltaic structure.

The transport layers, like the absorbent layer, also influence the performance of the device, parameters such as layer thickness, homogeneity, surface coverage, morphology, crystal quality, contact quality of the different functional layers, the density of defects, etc must also be optimized to improve efficiency.

Figure 17. Layout of the layers in the perovskite solar cell

Table 3. Some inorganic materials for electron transport (inorganic ETM) [64, 68 – 75]

Inorganic ETM			
ETM	Name	Ev/ Ec	gap
TiO ₂	Titanium dioxide	Ev = - 7.4eV, Ec = - 4.2 eV	3.2 eV
SnO ₂	Tin dioxide	Ev = - 8 eV, Ec = - 4.5 eV	3.5 eV
ZnO	zinc oxide	Ev = - 7.6 eV, Ec = - 4.4 eV	3.2 eV
In ₂ O ₃	Tin dioxide	Ev = - 8.2 eV, Ec = - 4.5 eV	3.7eV
CdSe	Cadmium selenide	Ev = - 5.8 eV, Ec = - 3.7 eV	2.1 eV
CdS	Cadmium sulfide	Ev = - 6.92 eV, Ec = - 4.5 eV	2,42eV.
Zn ₂ SnO ₄	Zinc stannate	Ev = - 7.8 eV, Ec = - 4.1 eV	3.7 eV
BaSnO ₃	Barium stannate	Ev = - 7.01 eV, Ec = - 3.91 eV	3.1 eV

Table 4. Some organic materials for electron transport (organic ETM) [68 – 70]

Organic ETM				
ETM	Name	Formula	Structure	HOMO/LUMO
PCBM	[6,6]-Phenyl-C61-butyric acid methyl ester	C ₇₂ H ₁₄ O ₂		HOMO = -6.1 eV, LUMO = -3.7 eV
C60	(C60-Ih)[5,6]fullerene	C ₆₀		HOMO = -6.2 eV, LUMO = -4.5 eV
IC60BA	indene-C60 bisadduct	C ₇₈ H ₁₆		HOMO = -6.5 eV, LUMO = -3.7 eV

Table 5. Some inorganic materials for hole transport (inorganic HTM) [71 – 81]

Inorganic HTM			
HTM	Name	Ev/Ec	Gap
CuI	Copper(I) iodide	Ev = -5.2 eV, Ec = -2.1 eV	3.1 eV
CuSCN	Copper thiocyanate	Ev = -5.3 eV, Ec = -1.7 eV	3.6 eV
NiO	Nickel oxide	Ev = -5.26 eV, Ec = -1.46 eV	3.8 eV
CuGaO ₂	Copper gallium oxide	Ev = -5.29 eV, Ec = -1.71 eV	3.58 eV
V ₂ O ₅	Vanadium pentoxide	Ev = -4.7 eV, Ec = -2.3 eV	2.4 eV
MoO ₃	Molybdenum oxide	Ev = -5.3 eV, Ec = -1.8 eV	3.5 eV

Some transport layers alone may be insufficient to achieve high yields due to low conductivity or other issues. Certain compounds called additives or dopants can be added to the transport layer to improve its charge conductive properties, to reduce (or eliminate) recombination in the HTM or ETM / absorbent layer interface, to optimize the stability and the performance of the cell. For example Lithium or cobalt salts are often used for p-doping to increase the concentration of holes. The Bis (tri fluoromethane) sulfonimidelithium (Li-TFSI) Li-TFSI salt is often used as a p-dopant to improve the conductivity and mobility of holes in Spiro-OMeTAD and -4-tert-butylpyridine (TBP) to suppress recombination of charges [90 – 91].

However, the additives can also cause detrimental drawbacks to the performance and stability of the cell by causing the degradation of the perovskite layer, especially with the infiltration of external moisture into the encapsulation of the cell if they have properties hygroscopic (which tends to absorb moisture). In table 8 we present some additives used with certain transport layers in PSCs.

Figure 18 shows the energy diagram of some perovskites.

Table 6. Some organic materials for hole transport (organic HTM) [64, 68, 82 - 88]

Organic HTM				
HTM	Name	Structure	HOMO/ LUMO	Gap
spiro-OMeTAD	2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene		HOMO = -5.2 eV, LUMO = -2.5 eV	2.7 eV
PEDOT: PSS	poly(3,4-ethylene dioxythiophene) poly(styrene sulfonate)		HOMO = -5.2 eV, LUMO = -3 eV	2.2 eV
PTAA	poly[bis(4-phenyl)(2,5,6-trimethylphenyl)amine] (PTAA)		HOMO = -5.1 eV, LUMO = -1.8 eV	3.3 eV
P3HT	poly(3-hexylthiophene-2,5-diyl)		HOMO = -5.2 eV, LUMO = -3.2 eV	2 eV

PCBTDP	poly [N-9-heptadecan-2-yl-2,7-carbazole-alt-3,6-bis(2,5-dioctyl-2,5-dihydro-1,4-dione)]		HOMO = -5.44 eV, LUMO = -3.92 eV	1.52 eV
PTB7	poly[[4,8-bis((2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)[3-fluoro-2-((2-ethylhexyl)carbonyl)thieno[3,4-b]thiophenediyl]]		HOMO = -5.15 eV, LUMO = -3.3 eV	1.85 eV

Table 7. Scaffolding materials and electrodes [68]

Scaffolding material	Metal electrode	Transparent electrode
Al ₂ O ₃	Ag	ITO
ZrO ₂	Au	FTO
SnO ₂	Ni	
ZnO	Cu	
TiO ₂	Al	
	C	

Table 8. Some additives used with certain transport materials in PSCs [64, 92 – 98]

Additive	Transport material	Effect
BCN: bamboo-structure carbon nanotubes	-P3HT	-improves crystallinity and mobility - improves the transfer of charges between the absorbent layer and the HTM
"bis (tri fluoromethane) sulfonimidelithium salt": Li-TFSI	-P3HT -spiro-OMeTAD	-to improve transport properties - to increase the concentration of holes - to improve conductivity and Mobility of holes - improved operation - improve HTM performance compared to devices without additives
4-tert-butylpyridine : TBP	spiro-OMeTAD	-to eliminate charge recombination
N-butyl-N - (4-pyridylheptyl) imidazolium bis (trifluoromethane) sulfonimide : BuPylm-TFSI	spiro-OMeTAD	- to simultaneously improve the electrical property of HTM and eliminate the recombination of charges

Note :

A material is considered ETM or HTM depending on the arrangement of the energy bands. However, the notion of ETM or HTM material can be considered to be relative. The behavior of an ETM or HTM material depends on its energy band configuration in the photovoltaic structure.

Figure 19 illustrates the energy band diagram of some materials.

Figure 18. Energy diagram of some perovskites, adapted from data of [89]

Figure 19. Energy band diagram of some materials, adapted from data of [101]

The transfer of charges takes place according to a structure similar to that shown in Figure 20:

Figure 20. Diagram of a perovskite solar cell, adapted of [102]

FTO/TiO₂/Perovskite/Spiro/Au (Cathode/ETM/Perovskite/HTM/Anode)

IV.4 Techniques of layer deposition

Different methods of deposition of hybrid perovskites with organometallic halides ABX₃ are reported in the literature with the aim of improving the quality of thin layers (control of the thickness, morphology, grain size, surface coverage, etc.) which is one of the key factors for the manufacture of high-performance photovoltaic devices [31, 11, 103]. High power conversion efficiency requires high quality perovskite films with suitable morphology, crystallinity, uniformity, phase purity and good photoelectric property. All of these requirements also depend on the method of synthesis, the composition of the precursors, the selection of solvents, the manufacturing environment, etc. [16].

The deposition of hybrid perovskite films with organometallic halides is generally based on the reaction [104] of BX₂ with AX in stoichiometric proportion, resulting in ABX₃, with X = I, Cl, Br; A = MA, FA, Cs; B = Pb, Sn.

Depositions of the perovskite layer are generally done in one or two stages by solution processes, vapor phase processes or a combination of these [104, 105]. Among the different synthesis methods, we can cite without being exhaustive: spin-coating, depositions in two sequential steps, vapor phase-assisted solution processes, vacuum deposition with two sources, chemical vapor deposition [106 - 118], etc. However, the

thin layers of perovskites synthesized by these techniques are multi-crystalline and generally influence the properties of material transport.

IV.4.a One-step methods

One-step methods are based on the co-deposition of precursors through a solution process or a vapor process.

1) One-step spin-coating

Spin-coating is a technique widely used for the preparation of APbX_3 perovskite films (MAPbI_3 or $\text{MAPbI}_{3-x}\text{Cl}_x$) because it saves time (it takes a few minutes), it is easy to use and can deliver good quality films. Two coating routes are possible with this technique : spin-coating in one step and spin-coating in two steps [119].

For the one-step spin-coating technique as illustrated in Figure 21, the precursors AX ($\text{A} = \text{CH}_3\text{NH}_3$, $\text{CH}(\text{NH}_2)_2$, Cs and $\text{X} = \text{I}$, Br, Cl) and PbX_2 ($\text{X} = \text{I}$, Br, Cl) are dissolved in a suitable solvent to obtain a mixed solution of precursors. The solution can be kept for several hours at room temperature or with heating before deposition until a limpid solution is obtained. Then the first step consists in depositing a small quantity of the precursor solution on the previously cleaned and treated substrate, placed on the plate of a spinner. The second step occurs when the substrate rotates, under the effect of the rotational speed, the solution spreads out and then forms a thin film. In this step, an additional solution, a solvent, an anti-solvent or additive can be deposited on the substrate if desired. Step 3 involves evaporating the solvent from the thin film. Depending on the solvent used, this evaporation can be obtained at room temperature, or the film can be annealed at a temperature (not very high so as not to degrade the perovskite) to complete the crystallization and evaporate the solvent residues. This technique can be carried out under ambient conditions or in a glove box filled with nitrogen [11, 16, 26, 31]. Perovskite crystallizes when the solvent evaporates during the rotation of the substrate or after annealing. The morphology of the layer obtained is often influenced by the annealing temperature [16].

For example to growth the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ with this technique, the organic halide $\text{CH}_3\text{NH}_3\text{I}$ and the lead halide PbI_2 are generally the precursors, they are dissolved in a suitable solvent such as N, Ndimethylformamide (DMF), gamma-butyrolactone (GBL) or dimethylsulfoxide (DMSO) to obtain a mixed solution of precursors ($\text{CH}_3\text{NH}_3\text{I} + \text{PbI}_2$) / DMF (or GBL or DMSO) maintained at approximately 70 °C before deposition. Then a small amount of the precursor solution is deposited on the substrate which is fixed on the spinner, this solution spreads out forming a thin film following the speed of rotation of the plate. This step is followed by annealing at 100 °C

for about 70 minutes on a hot plate to complete crystallization of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite formed. The same result is obtained with $(\text{CH}_3\text{NH}_3\text{X} + \text{PbX}_2) / \text{DMF}$ (or GBL or DMSO) for the formation of the perovskite MAPbX_3 ($\text{X} = \text{Br}, \text{Cl}$) by doing a similar process.

Figure 21. Spin coating a thin film on a substrate involves depositing a solution while the substrate is stationary (step 1) and / or rotating (step 2), followed by evaporation of the solvent (step 3), adapted of [26]

Regarding the ratio of precursors, in the case of no mixed APbX_3 perovskites such as MAPbI_3 , the stoichiometric proportion of the precursors MAI (AX) and PbI_2 (PbX_2) dissolved in an organic solvent for deposition by centrifugation, is generally (1 : 1) [25, 120]. While for the case of mixed perovskites like $\text{MAPbI}_{3-x}\text{Cl}_x$, the ratio is not equimolar, for example we can have $\text{MAI} : \text{PbCl}_2$ ($n : 1$) ratios with $n = 3, 4$, etc. [121,122].

2) Vapor deposition

In addition to the one-step solution treated methods, a one-step vapor phase method has also been developed for the growth of high quality perovskite films, this is dual source thermal evaporation. As illustrated in Figure 22, in this method the substrate is fixed in the upper part of the deposition system, while the precursors such as the solid salts, $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 (AX and PbX_2) are separately and simultaneously evaporated to form a film of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ (APbX_3) on the substrate. Then the heat treatment by annealing will help crystallize the perovskite layer. Thermal evaporation provides thickness control and produces better uniformity of perovskite films, resulting in good performance in photovoltaic devices. This method requires a high vacuum.

Figure 22. Preparation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films using vapor deposition methods: two-source thermal evaporation using sources of PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$, adapted of [123]

3) Hot Casting

For Hot Casting method (Figure 23), a mixed solution containing the precursors PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ is heated to 70°C and is deposited by spin coating on a substrate maintained at a temperature up to 180°C higher than the temperature crystallization of perovskite for a few seconds [31, 34]. This method produces a dense perovskite film with micrometer-sized grains [124] and does not require post-annealing treatment.

Figure 23. Hot casting deposition method, adapted of [31, 34]

Table 9. Some additives in the perovskite layer [125 – 128]

Additive	Step of deposit	Effect
1,8-diiodooctane (DIO)	In the solution of perovskite precursors	Film much smoother and better covered
toluene	during spin-coating of the perovskite precursors in the mixture of GBL and DMSO	Allows to obtain uniform and dense perovskite films
Second solvent : Chlorobenzene, toluene, diethyl ether	After deposition of the precursor solution during the spin-coation	-reduces perovskite solubility -induces perovskite crystallization --improves nucleation and rapid growth of perovskite crystals -dense film formation

IV.4.b Two-steps methods

The two-step deposition methods allow independent control of the deposition conditions of each precursor which ultimately allows better control of the perovskite film formation process. The two-step perovskite synthesis process can be done in different ways.

1) PbX_2 films in a MAX solution: Spin coating followed by soaking or Dip-coating

First, the inorganic thin film PbX_2 is deposited on a substrate by spin coating or by simple thermal evaporation and then this film is soaked in a solution containing the organic salt MAX (or the compound AX) for example (Figure 24). The solvent used for the solution containing the organic part is chosen so that it dissolves the organic salt MAX (or the compound AX) without affecting the inorganic film PbX_2 formed or preventing the formation of the perovskite MAPbX_3 [26].

For example in the case of the MAPbI_3 perovskite, the PbI_2 powder is generally dissolved in dimethylformamide (DMF) and the organic cation in 2-propanol (or in isopropanol IPA). The thin film of PbI_2 deposited on a substrate is soaked in the solution of MAI dissolved in 2-propanol for a certain time (a few seconds to a few minutes) at room temperature, then rinsed with 2-propanol and dried at 70°C for 30 minutes [129 – 131]. By varying the immersion time, the size of the perovskite grains and the roughness of the surface can be controlled. For example to obtain a layer thicker, the PbX_2 film must be left to soak longer in the solution containing the organic cation [132]. This technique allows dense films to be obtained, without pin-holes and with a recovery rate close to 100%, which results in high efficiencies [133].

Figure 24. Schematic representation of the sequential deposition of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ Film, adapted of [131]

2) vapor-assisted solution process (VASP)

A vapor-assisted solution process (VASP) has been developed for the manufacture of perovskite film (Figure 25), in which PbI_2 is deposited by centrifugation from a solution and then annealed in an MAI vapor to form MAPbI_3 films with a very smooth surface and full coverage [134].

3) Chemical Vapor Deposition (CVD)

Still taking the example of MAPbI_3 , the process consists of depositing a film of PbI_2 on a suitable substrate by thermal evaporation under vacuum, followed by deposition of

MAI in the vapor phase (Figure 26). The films obtained are generally of good crystalline quality, homogeneous with an average grain size of up to a micrometer [31,135].

Figure 25. Diagram for the assisted vapor phase process, adapted of [134]

Figure 26. Diagram for chemical vapor deposition in two steps, adapted of [135]

4) Two-step spin-coating

For the example of MAPbI_3 , before deposition by spin-coating in two steps, the precursors PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ are dissolved in N, N dimethylformamide (DMF) and anhydrous isopropanol respectively. In the first step, the PbI_2 solution is first centrifuged on the substrate and dried on a hot plate at approximately 70°C . Then, the $\text{CH}_3\text{NH}_3\text{I}$ solution is centrifuged on the PbI_2 layer (Figure 27), followed by an annealing procedure at 100°C for about an hour which allows the evaporation of the excess of the solvent (IPA) and better crystallization of the perovskite MAPbI_3 [16, 135].

Figure 27. Schematic diagram of the two-step spin coating method for the preparation of the perovskite film, adapted of [136]

However, it should be noted that there are other deposition techniques such as Spray Coating, Blade Coating, Slot Die Coating, Brush Painting, Electrodeposition, Ink-Jet Printing, Physical Vapor Deposition [137].

IV.4.c Synthesis of crystalline block (wafer) of perovskite

The process of crystallization of a target compound in a solution is defined as the formation of solids with properties of a solution where the solubility of the target compound (which will crystallize) is limited to a certain temperature leading to a supersaturated solution where the crystals will start to nucleate and grow. In addition to thin-film processing techniques, high-quality crystalline perovskite crystal block growth methods with excellent charge transport properties have been developed. Among these different methods we can cite inverse temperature crystallization (ITC)

and antisolvent vapor-assisted crystallization (AVC). There are also other methods of crystallization.

1) Inverse temperature crystallization (ITC)

Inverse Temperature Crystallization (ITC) is a method of rapidly synthesizing good quality perovskite crystals in a short time. In general, by decreasing the temperature of a solution, the solubility of a compound decreases, thus the material crystallizes. While in the case of this method (ITC), crystals are formed by heating the solution [31]. Indeed with this technique (ITC) there is a phenomenon of inverse solubility, that is to say that the solubility of the compounds decreases sharply when the temperature increases [16].

In this method as illustrated in Figure 28, a solution containing precursors of the perovskite $\text{CH}_3\text{NH}_3\text{PbX}_3$ is introduced into a flask or container then heated and maintained at a certain temperature which depends on the solution. After certain hours it crystallizes, forming a block of perovskite. For example, this precipitation phenomenon is observed for the perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$, the precursors of which PbBr_2 and $\text{CH}_3\text{NH}_3\text{Br}$ are dissolved in N, N-dimethylformamide (DMF). The solution containing these precursors is introduced into a flask immersed in an oil bath to be heated and the solution is maintained at approximately 80 °C to initiate crystallization [16, 137].

This same crystallization phenomenon is obtained for perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, the precursors of which PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ are dissolved in gamma-butyrolactone (GBL). Therefore, if the solution is kept at an elevated temperature of around 110 °C for a few hours, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal will precipitate and develop gradually [16].

The solubility of perovskite compounds would vary with solvents, $\text{CH}_3\text{NH}_3\text{PbI}_3$ exhibits better crystallinity in gamma-butyrolactone (GBL), while $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystallizes more in N, N-dimethylformamide (DMF). However, for $\text{CH}_3\text{NH}_3\text{PbI}_3$ / GBL and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ / DMF solutions, an inverse solubility phenomenon is observed, that is to say that their solubility decreases sharply when the temperature increases respectively from 60 °C to 110 °C for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and from 25 °C to 80 °C for $\text{CH}_3\text{NH}_3\text{PbBr}_3$. The crystallization temperature can also be influenced by the concentration of the precursors in the solution [16, 138].

Figure 28. Schematic illustration of the ITC method. The crystallization vial with the solution inside is immersed in an oil bath, heated to room temperature and maintained at an elevated temperature (80 °C for MAPbBr₃ and 110 °C for MAPbI₃) to initiate crystallization, adapted of [138]

2) Antisolvent Vapor-assisted Crystallization (AVC)

Antisolvent Vapor-assisted Crystallization (AVC) is a process of crystal formation by diffusion of anti-solvent. This method is easy to use and control and does not require heating. A suitable anti-solvent in which the perovskite is not soluble diffuses its vapor slowly in a solution containing the precursors of the perovskite and results in the formation of MAPbX₃ crystals as shown in Figure 29.

For example, for the case of perovskite CH₃NH₃PbBr₃, the precursors PbBr₂ and CH₃NH₃Br are dissolved in N, N-dimethylformamide (DMF) to give a CH₃NH₃PbBr₃/DMF solution. Then, the crystallization vial containing this solution is immersed without sealing in dichloromethane (DCM), an anti-solvent having a very low dissolution of perovskite MAPbX₃. Gradually, with the vapor of the anti-solvent slowly diffusing into the solution, the perovskite CH₃NH₃PbBr₃ crystallizes and grows [16,137]. The result is the same for the iodinated perovskite CH₃NH₃PbI₃ in the gamma-butyrolactone (GBL) of the CH₃NH₃PbI₃ / GBL solution.

Figure 29. Schematic diagram of the crystallization process, adapted of [137]

IV.4.d Manufacture example of a perovskite solar cell

Case of a mesoporous cell architecture : Cathode / ETL / Scaffolding / Perovskite / HTL / Anode

Example: FTO / c-TiO₂ / m-TiO₂ / Perovskite / Spiro-OMeTAD / Ag

Manufacture of the device [26] :

1- Transparent collecting electrode FTO : cathode

One can use a fluorine-doped tin oxide substrate (FTO, SnO₂ : F) pre-etched and then cleaned in an ultrasonic bath, demineralized water, and isopropanol solution for about 20 minutes.

2 - ETL / scaffolding : compact layer of TiO₂ / mesoporous layer of TiO₂

- A compact layer of TiO₂ can be deposited by spin coating (Figure 30-a), for example titanium diisopropoxide bis (acetylacetonate) diluted in 1-butanol, at 4000 rpm for 40 s.

- A mesoporous layer of TiO₂ can be deposited (Figure 30-b), for example, via a paste of TiO₂ diluted in ethanol in a ratio of 2 : 7, then coated by centrifugation at 4000 rpm for 40 s. Then the substrate is dried at 125 °C for 5 min and annealed at 500 °C for 30 min.

Figure 30. Deposition of : (a) compact layer of TiO₂ / (b) mesoporous layer of TiO₂

3- Deposition of perovskite

For a two-step deposition of the perovskite layer :

- for example, for MAPbI₃, a solution of PbI₂ in DMF can be used, stirred at 70 °C and deposited by spin-coating at 5000 rpm for 40 s (Figure 31-a). This film is then dried at 70 °C for 10 min.

-During the spinning process at about 1500 rpm, a solution of MAI in isopropanol can be poured onto the substrate for a period of 20 s. Then the film is annealed at 100 °C for 30 min to complete the formation of the perovskite film (Figure 31-b).

Figure 31. Deposition of perovskite layer (MAPbI₃) in two step method ((a) and (b))

4- Deposition of the HTL : hole transport layer

For the deposition of the hole transport layer, a solution of 4-tert-butylpyridine and one of lithium bis (trifluoromethane) sulfonimide salt which are additives, can be added to a

solution containing 2, 2' , 7 , 7'-Tetrakis- (N, N-di-p-methoxyphenylamine) 9,9'-spirobifluorene (Spiro-OMeTAD). This solution can be deposited on the substrate by spin-coating at 4000 rpm for 40 s (Figure 32).

Figure 32. Deposition of hole transport layer (Spiro-OMeTAD)

5- Deposition of the metal contact : Anode

100 nm of gold (Au) or silver (Ag) can be evaporated as the upper electrode (Figure 33). The operating perovskite solar cell is shown in Figure 34.

Figure 33. Deposition of metal contact (Au)

Figure 34. Operating perovskite solar cell

IV.5 Hysteresis in perovskite solar cells

Figure 35. Hysteretic behavior in perovskite solar cells, adapted from data of [139]

Although organometallic halide perovskite-based solar cells have shown promising efficiency, there are still some problems to be solved for their large-scale application such as stability and hysteresis [104].

Hysteresis is a phenomenon commonly observed during performance tests by measuring the J-V (current density – voltage) characteristics of perovskite solar cells

(mesoscopic and planar) [68]. This is a difference (offset) noted in the J-V curve. Indeed, the J-V curve plotted by increasing the values of V (forward) is different (shifted) from that obtained by decreasing the same values of V (reverse) (see Figure 35). This offset of the curves is a function of the sweep conditions of the variation in the values of V in the measurement (sweep direction, sweep speed, light soaking, polarization) and of the architecture of the cell and its composition (materials of transport and contact electrodes) [140 - 145].

This hysteresis phenomenon has also been detected in DSSC, CIGS, CdTe and amorphous silicon solar cells, OPV cells [68,140,146 - 149] and can be remarkably suppressed by a slow scanning speed in these types of solar cells [68]. It is only with perovskite solar cells that this abnormal phenomenon is more frequent and a severe change on the efficiency is observed.

Thus the very rapid increase in the efficiency of perovskite solar cells has raised many questions about the measurement process, since current-voltage measurements show ambiguous efficiency values following the measurement procedure. The consequence is that the efficiency value can be overestimated if the scanning speed is too high for the cell to reach its permanent electronic equilibrium. This means efficiency measures should always be treated with caution.

For the precise measurement of perovskite solar cells, it is usually necessary to include the data from the forward and reverse J-V curves at different scan rates as well as the constant state of the photocurrent at voltages near the point of maximum power (P_{max}) when yields are reported [150].

The hysteresis in PSCs reflects the efficient or inefficient extraction of photogenerated charge carriers through the transport layers. Several possible ideas (hypotheses) have been proposed as a cause to explain this phenomenon of hysteresis in perovskite solar cells, including trap states resulting from a large density of defects inside or in proximity to the surface of the material, ferroelectric properties or behaviors and ion migration due to excess ions which serve as interstitial defects [151 – 155].

1) Ferroelectric behavior

Ferroelectricity is the property according to which a material has a spontaneous electrical polarization which can be reversed by the application of an external electric field. The signature of a ferroelectric material is the hysteresis cycle of the polarization as a function of the applied electric field (P-E).

The polarization (or existence of electric dipoles) of organometallic halide perovskite materials has been reported both theoretically and experimentally, as well as their ferroelectric properties [156 – 158].

Based on the existence of ferroelectricity, there are established models to explain the hysteresis behavior in perovskite materials. When applying an electric field, as shown

in Figure 36, the dipoles due to the rotation of the MA group or the distortion of the inorganic cages, are aligned following the direction of the external field (in the same orientation or in the opposite orientation). This dipole alignment process generates a compensated field, that is, a field of depolarization. This process significantly influences the effective potential drop by increasing or decreasing the separation of charge carriers in the material. This modulation of the internal electric field reflects the efficient or inefficient extraction of photogenerated charge carriers through the transport layers and therefore, can lead to the hysteresis of the J-V measurement [159 - 160].

However, although the ferroelectricity model has attempted to explain the behavior of hysteresis in PSCs, it still suffers from several arguments. There is still controversy in identifying the existence of ferroelectric properties in organometallic perovskites. The decay of the depolarization field is very fast and it would have an absence of the standard P-E hysteresis loop. The polarization switching timescale does not agree with that observed in the J-V hysteresis curve [161 - 162]. Therefore, although the contribution of ferroelectricity to the hysteresis is still under debate, the ferroelectric effect is too weak to be convincing and that ferroelectric polarization cannot play the dominant role in the behavior of J-V hysteresis in PSCs [159].

2) Effects of defects

Another mechanism that is probably the cause of the observed hysteresis is the presence of a very large concentration of defects located in bulk, on the surface or at the interface of the material. The conditions for the synthesis of perovskite films inevitably also involve Certain defects in the lattice, namely vacant positions (V_{MA} , V_{Pb} , V_I), anti sites (Pb_{MA} , MA_{Pb} , MA_I , Pb_I , I_{MA} , I_{Pb}) and interstitial sites (I_{MA} , I_{Pb} , I_I) [164] which can introduce an energy distribution in the forbidden band [165]. The traps are mostly accumulated at the interface or on the surface, where there is a break in the periodicity of the crystal lattice. A large quantity of the trap states is due to the small grain sizes because they generate more grain boundaries and interfacial zones acting as trapping sites. These states could act as traps for electrons and holes. This mechanism could well explain why the hysteretic behavior strongly depends on the architecture, because the latter directly influences the times of trapping and withdrawal of charges in defects linked to interfaces and surfaces.

Thus the charge trapping and de-trapping process [166 - 167], consisting in filling and freeing the trap sites (defects), leads to a modulation of the transport of photogenerated charges and of the performance of the devices, and consequently , may explain the hysteretic behavior.

Figure 36. Band diagram due to the influence of ferroelectric polarization on the internal field, adapted of [163]

However, taking into account these defect states, it is natural to compensate or fill them by using different methods of synthesis or passivation process [168] :

- Passivation of the interfaces and the trap states (grain boundaries) in the perovskite significantly reduces the hysteresis, improves the transport and extraction of charges.
- Various scientific groups have reported that a perovskite film with large grain sizes shows negligible hysteresis regardless of the architecture of the cell. In other words, the larger grain size induces fewer defects on the surface or at the interface of materials
- Very recently, it has been shown that the reduction of the density of the interfacial trap thanks to an improved synthesis of perovskite solar cells can considerably reduce the hysteretic behavior of PSCs.

Although the process of passivation (and reduction of interfacial states) considerably improves performance and decreases hysteresis, it is observed that the time interval for charge trapping and de-trapping varies in milliseconds, even in nanoseconds,

which is much shorter than the typical time for the hysteretic behavior [169 – 170]. Moreover, the great difference observed in the variation of the photocurrent and the slowness of its evolution after polarization cannot be explained by the mechanism of trapping of the charges only [171]. Therefore, some believe rather that of a single origin, the hysteresis must be due in terms of a combined factors, including both ionic migration in addition to the effect of trapping and withdrawal of charges and the ferroelectricity.

3) Ionic migration

Ion migration is considered to be the dominant factor associated with hysteresis [172]. The observation of the migration of ions in the perovskite layer by various experimental methods suggested that this phenomenon could be at the origin of the current-voltage hysteresis. The species that can be at the origin of these migrations in MAPbI₃ PSCs are iodide I⁻ ions, methylammonium or MA⁺ ions, H⁺ hydrogen ions and Pb²⁺ ions [173 – 174]. These ions come from defect states during manufacturing, such as vacancies (V_{MA}, V_{Pb} et V_I), interstitial sites (I_{MA}, I_{Pb}, I_I), antisites (Pb_{MA}, MA_{Pb}, MA_I, Pb_I, I_{MA}, I_{Pb}), etc. [175]. H⁺ ions come from the low acidity of MA⁺.

However, the extent of each ion's contribution to hysteresis is still under debate. Theoretical and experimental studies on the dynamics and kinetics of ion migration made by certain authors reveal that the diffusion of iodides I⁻ and MA⁺ are mainly responsible to the hysteresis. These studies also suggest that the diffusion of MA⁺ is negligible compared to that of I⁻ due to a significant drop of the diffusion coefficient (10^{-16} V.cm² s⁻¹ for MA⁺ vs. 10^{-12} V.cm² s⁻¹ for I⁻) [68]. Iodide ions I⁻ are the most mobile and would have a more important role in the cause of hysteretic behavior compared to MA⁺ ions. The measured diffusion coefficient of the ions, which are responsible to the hysteresis in MAPbI₃, is estimated to be around 10^{-11} to 10^{-12} V.cm² s⁻¹ [176 – 177]. The estimated value of the MA⁺ ion diffusion coefficient (in the order of 10^{-16} V.cm² s⁻¹) is much lower than the coefficient predicted by [176 – 177]. Only the diffusion coefficient of the iodide ion is evaluated in this order of magnitude estimated by [176 – 177], which suggests that iodide I⁻ ions would be the main reason of the hysteretic behavior. H⁺ ions seem to have a minor role compared to other defects (I⁻ and MA⁺), their concentration is not high because of the low acidity of methyl ammonium (MA⁺).

Transport for ion migration is supposed to be facilitated in part by a jump mechanism through the lattice of atoms assisted by point defect states (vacancies, interstices) and other possibilities of migration channels such as grain boundaries where the diffusivity would be higher [173,178]. Thus, the movement of ions in the material is made possible by the existence of point defects.

The process of hopping between neighboring sites requires energy, ie activation energy E_a to overcome the barriers. This hopping process is highly temperature dependent, it is described as a thermally activated point defect movement. The activation energy E_a strongly depends on the ionic species. It is possible to obtain E_a by various experimental measurements or on the basis of theoretical calculations. The activation energy E_a increases with grain size, single crystals have a higher activation energy than polycrystals. Experimental and theoretical studies generally show a low energy of defect formation for I^- ions (0.58 eV) compared to those of MA^+ (0.84 eV) and Pb^{2+} (2.31 eV) [80]. The significantly higher activation energy of Pb^{2+} indicates that such migration seems unlikely, suggesting that I^- and MA^+ ions play a major role in hysteresis rather than Pb^{2+} ions.

Thus the slow response times (in the order of tens of ms in minutes) generally observed with the hysteresis in perovskite solar cells deemed unexplained by the hypothesis of trapping and de-trapping of charges or ferroelectricity, could well be explained by the slow migration of MA^+ (or Pb^{2+}) ion defects given their low diffusion coefficients and their higher activation energies. Migration of iodide defects is probably very rapid to explain the slow responses often found in solar cells.

Also the theory based on the ion defect migration mechanism has also been suggested to be the cause of the reduction of the hysteresis for a fast scanning because the defects have less time to migrate to the interfaces (or electrodes).

Following their migration under the effect of an external electric field (field resulting from polarization), the ions accumulate near the contacts between the perovskite and the transport layers (perovskite / ETL and perovskite / HTL), The negatively charged ions I^- migrate in the opposite directions of the external field (polarization field) and the positively charged ions MA^+ in the same direction (see Figure 37), their redistribution depends on the polarization voltage. This accumulation of space charge near the contact leads to significant band bending and thus influences the extraction of generated charges [179]. It causes a variation of the internal field in the perovskite and a modulation of the interfacial barriers thus giving rise to the hysteretic behavior which could lead to various J-V characteristics.

In fact, the positive and negative charges accumulated at the opposite interfaces generate an additional electric field in the device. This field can improve or decrease the original field and therefore the separation of photogenerated charges can be improved or deteriorated [177]. The modulation of the interfacial barriers by the accumulation of charges results in an influence on the injection and extraction of charges, so the efficient process of charge transfer through these interfaces can be modulated by the ions, which are entrained by the external electric field.

Figure 37. Diagram showing ionic migration under external electric field, adapted of [180]

To eliminate the hysteresis caused by the phenomena of ion migration, it seems useful to reduce defect states, decrease the migration of ions and promote the process of charge transfer at the interfaces. Devices with larger grain sizes exhibit low hysteresis behavior. In fact, a larger grain size decreases the defect states and makes it possible to reduce the migration canals generated by the small grain sizes. Passivation of the layers and interfaces by means of suitable additives presents much less hysteresis (for example PCBM). The incorporated additives can be absorbed at the defective sites of the perovskite in the vicinity of the grain boundaries, their molecules can passivate the defect states or chemically combine with the defect ions by establishing chemical bonds in order to immobilize them, which can reduce the migration of ions in the perovskite layer. Passivation of surface and interface states with the additive also improves charge transfer through perovskite / transport layer contacts by reducing ion build-up and eliminating the establishment of interfacial barriers.

IV.6 Instability issue

Despite their good performance, perovskite solar cells initially suffered from big stability problems and degraded rapidly in the short term under the influence of oxygen, UV light, temperature (heat) and humidity. For instance MAPbI_3 degrades rapidly to produce lead iodide PbI_2 . To date, the degradation mechanism is not well understood but several mechanisms have been proposed to account for the phenomenon of degradation. Among solutions, mention the surface decoration of perovskites in order to stabilize the material, surface passivation, use of additive and encapsulation in particular using graphene. Concerning possible causes of degradation, one could be the formation of inactive clusters under the effect of incident light. If this mechanism is validated, the solution could be given by material engineering, that could also reduce another mechanism, the current limitation due to

structural defects, and be accompanied by band gap tuning. Attention should be also paid to the role of defects expected to exist following the fundamental studies of the softness of the considered crystalline structures. The intrinsic instability of PSCs was a major challenge but promising solutions have been found and continue to be explored in order to open the route to a more massive industrialization.

V. Conclusion

This chapter resumes numerous investigations of the photovoltaic properties of 3D perovskites based on lead halides APbX_3 ($X = \text{I}, \text{Br}, \text{Cl}$). These materials have generally a direct band gap with good photon absorption properties and exhibit good electric charge transport properties. Despite the possibility of substituting lead with other elements of the same degree of oxidation, the best photoconductive properties of perovskites 3D have so far been based on lead. However, the synthesis of mixed perovskites by partial substitution of cations (A and Pb) or anions (X) has extended the family of these photovoltaic absorbers and has given promising results in PV applications.

The easy production of PSCs is related to the low energy to form 3D perovskites, but the counterpart is the low stability. 2D perovskites were much less studied as materials for photovoltaics, but they could reveal good performances and better stability from the energetical point of view. However, despite the diversity of solar cells based on perovskites and their good performance, details of their operating mechanism remains little known. The hysteresis interpreted as being the cause of several degradation factors also poses a problem for accurate performance measurement. Once the problems of longevity of PSCs resolved, problems linked to their sensitivity to corrosion and humidity, to the formation of degradation products, to deterioration and lack of thermal stability of materials (the question of stabilizing performances of perovskite solar cells is considered in chapter 24 of this volume), perovskite solar cells will have all qualities to massively replace the other cells.

Perovskite-based solar cells exist in several architectures classified into two categories (mesoscopic and planar) with easy manufacturing techniques at low cost and a variety of materials for the transport of charges (electrons and holes) which just need to be favorable to a separation and good transfer of charges to produce electricity. The next step to a massive production is to continue translating the laboratory techniques to industrial ones, and in this respect the techniques of screen printing are being developed (see also chapter 15 of the present volume) opening the possibility to produce massively flexible and light PSCs. An important point is also to simulate ageing of cells to test their longevity that remains to be proved and compared to that of first generation cells that are observed to be still working after 25 years.

A tendency is also to produce tandem cells including a perovskite layer and perovskite-multilayer cells to reach higher efficiencies for a lower cost than with vacuum technologies.

It is noticeable that the field is in constant and rapid development, and the perovskite solar cells appear as the most promising cells to solve energy problems in the future.

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