Improving the stoichiometry in lead iodide and perovskite micro-crystals, towards the fabrication of more efficient perovskite solar cells

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Abstract

The technology of photovoltaics provides a renewable and ecofriendly way of conversion of photons to electricity. Low cost photovoltaics with high efficiency and extended life time are some of the main goals during their fabrication. Perovskite solar cells (PSC) have been promoted to potential candidates in the field of photovoltaics. In this thesis, chapter 1 provides a general background theory about the field of perovskites and their use to fabricate PSC. In chapter 2, experimental details are provided, supporting the work that was made and the relevant theory of characterization techniques used. Chapter 3, mainly focusing on a low-cost, energy efficient and water-free synthesis of lead iodide (PbI₂) a material widely used for the fabrication of perovskites, by planetary ball milling (mechanochemical), controlling both stoichiometry and number of polytypic phases. Chapter 4, focusing on the stability of PSC fabricated with an optimum stoichiometry between different ions present in the photoactive layer. Synthesis of controllably doped or undoped methylammonium lead triiodide (CH₃NH₃PbI₃) micro-crystals with various amounts of dopants of either methylammonium bromide (CH₃NH₃Br) or formamidinium iodide (CH(NH₂)₂I) or CH(NH₂)₂I and bromine (Br₂), was achieved. Characterization techniques used, included X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), atomic force microscopy (AFM), scanning electron microscopy (SEM), UV-Vis spectroscopy, controllable chemical synthesis of micro-crystals and testing operational PSC devices. The results presented in chapter 3, indicated that the use of the sub-stoichiometric PbI₂ (when iodine content is below the optimum 1 : 2 ratio of Pb : I atoms) during the fabrication of the photoactive layer in PSC devices, results in unreacted PbI₂. The presence of unreacted PbI₂ reduces the average power conversion efficiency (PCE) of the PSC from ~ 15.5 % to ~ 4.6 %. Whereas, the results presented in chapter 4, indicated that controllable doping of CH₃NH₃PbI₃ micro-crystals with different incorporated ions, reveals a minimum of distortion in the resulted perovskite crystal structure. That might lead to an optimum composition in perovskites with enhanced chemical stability as function of the exposed conditions. Un-encapsulated PSC devices fabricated using controllably doped CH₃NH₃PbI₃ micro-crystals, showed a reduction in the average PCE from ~14 (±1.5)% to ~13.7 (±0.5)%, after storage in dark and under ambient conditions for 240 hours.
Publications


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Chapter 1

Background theory

1.1 Introduction

Since the dawn of organic-inorganic perovskites as a new class of semiconductors, several researchers have been studying their optoelectronic properties through fabrication of devices, such as photovoltaics, light emitting diodes (LEDs), photodetectors, batteries or even in the field of spintronics. \(^1\)–\(^5\) Their scientific attractiveness originates from the low cost, the remarkable variability in optoelectronic properties as function of ratio between the mixed organic-halogen and their simplicity of fabrication process. In the first chapter, the broad motivation for research and the necessity of renewable sources of energy is described, emphasizing more in photovoltaic solar technologies. Specifically, a range of information are provided, building up a background on perovskite solar cells, such as, their main device architectures, types of defects, principles of operation and obstacles to their commercialization. Additionally, in this chapter attention is given to the topic of stoichiometry and polytypism in lead iodide and perovskite photoactive layer and its links to durability and stability, being the main motivations for that specific work presented here and puts it in context.
1.2 Motivation

1.2.1 Global warming

Energy demand is expected to increase in all realistic scenarios of the near future world-wide as estimated by the U.S. Energy Information Administration, International Energy Outlook 2017, as shown in figure 1.1, due to the rise of industrial activity, food production, services and increase of the global population. The primary natural energy sources, such as petroleum (and derivatives), coal and natural gas, have remained the main sources of energy for the last 29 years. However, growing concerns that have been triggered by the high emission of greenhouse gases such as carbon dioxide (CO₂), nitrous oxide (N₂O) and methane (CH₄), which inevitably leads to climate change and global warming, as stated by the IPCC (Intergovernmental Panel on Climate Change) and temperature global vs solar activity observations conducted by NASA/JPL-Caltech, as shown in figures 1.2 and 1.3. The challenge that we are facing is not only to terminate the consumption of our planet’s current sources of energy originated from fossil fuels, but to rely on technologies for power generation with lower emission of greenhouse gases and elevated degree of abundancy. The development of renewable sources of energy is widely expected to serve both these options. Global energy production based on renewable sources of energy such as wind, tidal, hydropower, geothermal, biomass and solar photovoltaic technologies (excluding nuclear fusion), show a stable steady pace of growth, as shown in figure 1.4 and reported by REN21 global status report (Renewable Energy Policy Network). However, even though primary installed infrastructures related to renewable sources of energy are suffering from prohibitive costs, optimization research in materials used and construction methods result in competitive options in comparison with the widely dominated market of fossil fuels sources of energy. In 2018 for example, the levelized cost per kWh of electricity produced (including materials, installation and land) related to large scale photovoltaic installations in Germany, was almost 20 % lower in contrast with the cost per kWh of electricity produced in facilities utilizing coal or natural gas, as provided by Fraunhofer Institute for Solar Energy Systems (ISE) and shown in figure 1.5. In 2017, only ~ 19 % out of the total global energy production originated from renewable sources of energy. Approximately, a share of 20 % out of the total renewable sources of energy, corresponds to photovoltaics, the same year. However,
is believed that a strong candidate for supplying all the global energy required could be provided solely by photovoltaics. Since the amount of incident solar energy that hits the Earth per hour is \( \sim 4.1 \times 10^{20} \) joules, while the total annual global consumed energy is \( \sim 4.3 \times 10^{20} \) joules (as provided by the World Energy Council). That could practically be translated, that if photovoltaics with power conversion efficiency of 15 % are evenly installed around the world, requires a total global land area of \( \sim 2 \) %, so that the annual global energy (electricity) production be fulfilled.

![Figure 1.1: World energy consumption by energy source from 1990 to 2040 (predicted). Source - U.S. Energy Information Administration, International Energy Outlook 2017](https://www.eia.gov/)

![Figure 1.2: Globally averaged greenhouse gas concentrations from 1850 to 2000. Source - IPCC (Intergovernmental Panel on Climate Change) (https://www.ipcc.ch/)](https://www.ipcc.ch/)
Figure 1.3: Earth temperature vs solar activity from 1880 to 2015. Source - NASA/JPL-Caltech (https://climate.nasa.gov/).

Figure 1.4: Global renewable power capacity from 2007 to 2017. Source - REN21 global status report (Renewable Energy Policy Network) (https://www.ren21.net/).
Figure 1.5: Levelized cost of electricity (Eurocent / kWh) produced by newly built infrastructures, based on renewable and fossil fuels sources of energy. Source: Fraunhofer Institute for Solar Energy Systems (ISE) (https://www.ise.fraunhofer.de/).

1.2.2 Renewable energy sources and photovoltaics

The constantly increasing global energy demand, combined with the rising emission of gases that are responsible for the greenhouse effect (CO$_2$ / N$_2$O / CH$_4$), has caused significant environmental and political concerns during the last two decades. Combined with the climate change, the importance of development towards a more environmentally friendly and viable mixture of global energy production sources, free of or with reduced dependency on fossil fuels, is a vital priority for humanity. So far, remarkable progress has been made at the academic and industrial level, exploring, investing and developing a range of renewable sources of energy, as shown in figures 1.6 and 1.7. The major fraction of investment and research, in comparison with all available renewable sources of energy, has been attributed to solar and wind technologies the last two decades. This is reflected by the abundancy of wind and solar irradiation, responsible of the extensive integration of these technologies in the
total mix of energy generation. However, solar photovoltaics consist an excellent choice as a renewable source of energy, since the low cost of fabrication, combined with the small environmental impact, display significant advantage, in comparison with wind power technologies.

**Figure 1.6:** Global number of patents per sector in renewable sources of energy from 200 to 2016. **Source** - International Renewable Energy Agency (IRENA) RE-source Database (EPO PATSTAT Database) ([https://ourworldindata.org/renewable-energy](https://ourworldindata.org/renewable-energy)).

**Figure 1.7:** Global investment in renewable sources of energy from 2004 to 2016. **Source** - International Renewable Energy Agency (IRENA) ([https://ourworldindata.org/energy](https://ourworldindata.org/energy)).
Since the fabrication of the first photovoltaic solar cell with power conversion efficiency ~ 6 %, based on doped silicon (Si) semiconductors to construct a p – n (junction), in Bell Laboratories in 1954, significant engineering attention was aroused improving their efficiency and properties. The following 6 decades, through steps of development in materials and engineering, successful fabrication of Si based solar cells with power conversion efficiency ~ 26.6 % was achieved. As such, Si is the leader in the field of photovoltaics, combining low cost of fabrication and moderate power conversion efficiencies. Additionally, exploitation of other configurations and materials as photoactive thin films, such as copper indium gallium selenide (CIGS), copper zinc tin sulfide (CZTS), cadmium telluride (CdTe), organic photovoltaics (OPV), quantum dot solar cells (QDSCs), dye-sensitized solar cells (DSSCs) and doped gallium arsenide (GaAs) in single or multi junctions, exhibited a range of power conversion efficiencies. However, over the last decade remarkable attention has been focused on perovskite solar cells (PSCs), due to the rapid increase in their power conversion efficiency (PCE) values (~ 24 %), as provided by NREL (National Renewable Energy Laboratory) and shown in figure 1.8. Note the much steeper gradient for the increase in PCEs for the perovskite curve.
Figure 1.8: Chart of the highest confirmed power conversion efficiencies of solar cells for a range of photovoltaic technologies. Source – NREL (National Renewable Energy Laboratory) (https://www.nrel.gov/pv/cell-efficiency.html).
1.3 Perovskite solar cells

1.3.1 Origin of perovskite semiconductor

Historically, the first perovskite structure described was the calcium titanate (CaTiO$_3$) mineral, that was discovered in the Ural Mountains by Gustav Rose in 1839 and its name was given in honour of the Russian mineralogist Aleksevich Lev Perovski. In the middle of the 1930s, Victor Goldschmidt first introduced the general chemical formula ABX$_3$, as the fundamental composition of perovskites and suggested the property of tolerance factor in ABX$_3$ formula. The family of materials obeying the perovskite formula, includes a large number of metal – oxide and metal – halide compounds. In the field of solar cell research, the most studied metal – halide compounds are well known as halide perovskites, in which A is a cation such as, methylammonium (CH$_3$NH$_3^+$), formamidinium (CH(NH)$_2$) or caesium (Cs$^+$), B being a post-transition metal, such as lead (Pb$^{2+}$), tin (Sn$^{2+}$) or bismuth (Bi$^{3+}$) (bismuth has got more than one oxidation state: - 3, + 1, + 2, + 3 or + 5) and X is a halogen anion such as, bromine (Br$^-$), chlorine (Cl$^-$) or iodine (I$^-$). The ideal crystal structure of halide perovskites at temperatures above 330 K is that with cubic symmetry, composed by a framework of corner shared octahedrons (BX$_6^-$) in three-dimensional space, as shown in figure 1.9.

Figure 1.9: (a) Crystal structure of perovskite with chemical formula ABX$_3$ and (b) unit cell of CH$_3$NH$_3$PbI$_3$ perovskite.
In 1958, Moller (a Danish scientist) discovered that CsPbI$_3$ crystallised in the perovskite structure and observed photoconductivity. In 1978, Dieter Weber, a German scientist, replaced the caesium with the methylammonium cation and synthesized the first organic – inorganic (hybrid) perovskite material, using either lead or tin. He also measured the absorbance band edge of these materials being around \(~800\) nm, implying their ability to act as photoactive materials.\(^{11,12}\) Also, David Mitzi successfully fabricated thin film transistors and light emitting diodes (LEDs), using hybrid perovskite materials, a few years later.\(^ {13,14}\) In 2009, the group of Miyasaka successfully fabricated for the first-time photovoltaics using methylammonium lead triiodide (CH$_3$NH$_3$PbI$_3$) hybrid perovskite as a photoactive material with power conversion efficiency \(3.8\) \%, based on the fabrication protocol used on DSSCs.\(^ {15}\)

Throughout the following decade, remarkable scientific progress was achieved at the field of hybrid perovskites, with the astonishing PCE of \(~23.6\) \% being reached using mixed cation / anion hybrid perovskites.\(^ {16}\)

### 1.3.2 Tunability and optoelectronic properties of perovskites

CH$_3$NH$_3$PbI$_3$ is one of the most studied hybrid perovskites, showing some remarkable optoelectronic properties. With a direct – indirect energy band gap of \(1.51 \sim 1.55\) eV, low exciton binding energy \((\sim 16\) meV), excitonic effective mass \(0.104* m_e\) (where \(m_e\) is the electron mass), long diffusion lengths for both electrons and holes \((0.1 \sim 1\) μm) and high charge (electrons / holes) mobilities.\(^ {17–22}\) All these combined parameters, result in efficient diffusion of charge carriers before being recombined, causing CH$_3$NH$_3$PbI$_3$ an excellent photoactive layer for fabrication of solar cells. However, due to its inferior stability under moisture and oxygen, more engineering steps were implemented to tackle that problem.\(^ {23,24}\) A mixture of more than one cation / anion at different ratios in hybrid perovskites results in extensive tunability of the energy band gap, with improved stability upon temperature, oxygen and moisture. Both these properties are primarily caused by the structural shift from orthorhombic or tetragonal to more symmetrical ones, such as the cubic crystal structure, due to the different values of the effective ionic radius for the A and X ions used in the general chemical formula $ABX_3$ of perovskites.\(^ {25}\) A range of different anions / cations have been used, for the fabrication of perovskites, as shown in table 1.1.\(^ {26}\)
<table>
<thead>
<tr>
<th>A - Cation</th>
<th>$r_A$ (pm)</th>
<th>B - Cation</th>
<th>$r_B$ (pm)</th>
<th>X - Anion</th>
<th>$r_X$ (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubidium [Rb]$^+$</td>
<td>149</td>
<td>Silver [Ag]$^{+2}$</td>
<td>94</td>
<td>Bromine [Br]$^-$</td>
<td>196</td>
</tr>
<tr>
<td>Hydroxylammonium [NH$_3$OH]$^+$</td>
<td>216</td>
<td>Bismuth [Bi]$^{-3}$</td>
<td>103</td>
<td>Iodine [I]$^-$</td>
<td>220</td>
</tr>
<tr>
<td>Caesium [Cs]$^+$</td>
<td>167</td>
<td>Tin [Sn]$^{+2}$</td>
<td>115</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylammonium [CH$_3$NH$_3$]$^+$</td>
<td>217</td>
<td>Lead [Pb]$^{+2}$</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrazinium [NH$_3$NH$_2$]$^+$</td>
<td>217</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Azetidinium [(CH$_2$)$_2$NH$_2$]$^+$</td>
<td>250</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formadinium [CH(NH$_2$)$_2$]$^+$</td>
<td>253</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imidazoline [C$_3$N$_2$H$_5$]$^+$</td>
<td>258</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-pyrollinium [NC$_4$H$_8$]$^+$</td>
<td>272</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylammonium [CH$_3$CH$_2$NH$_3$]$^+$</td>
<td>274</td>
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<td></td>
</tr>
<tr>
<td>Guanidinium [(NH$_2$)$_3$C]$^+$</td>
<td>278</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetramethylammonium [(CH$_3$)$_4$N]$^+$</td>
<td>292</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thiazolium [C$_3$H$_4$N$_3$]$^+$</td>
<td>320</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tropylium [C$_7$H$_7$]$^+$</td>
<td>333</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Effective ionic radius of $A$ – cations, $B$ – cations and $X$ – anions, for perovskites with chemical formula $ABX_3$. 26
Pellet et al. have shown that a mixture of FA⁺/MA⁺ cations results in a more stable perovskite FAₓMA₁₋ₓPbI₃ (with x ≤ 0.8). 27 While Choi et al. have shown that mixture of Cs⁺/MA⁺ cations leads to perovskite CsₓMA₁₋ₓPbI₃ with enhanced stability, free of the detrimental 2H yellow phase of lead iodide (PbI₂). 28 Also, due to the high toxicity of lead (Pb²⁺), as a B – cation in the chemical formula ABX₃ of perovskites, its replacement with tin (Sn²⁺), which is a less toxic metal in comparison with lead, results in PSCs with unfortunately lower values of PCEs ~ 9 %. 29 Also, due to the shift on the oxidation state of Sn²⁺ to Sn⁴⁺, after contact with oxygen, this results in PSCs with inferior lifetime. However, perovskites made with a mixture of Pb²⁺/Sn²⁺, have shown significant research attention. Since the mixture of Pb²⁺/Sn²⁺ has shown less toxicity, narrower band gap (~ 1.26 eV) and formatted perovskite with longer stability, might be an ideal candidate for the fabrication of single or tandem PSC devices. 30 On the halide side of perovskites with the ABX₃ chemical formula, substitution of iodine with bromine and / or chlorine, has also been investigated, in combination with either FA⁺ or MA⁺ cations. A higher amount of incorporated bromine, results in an increase of the energy band gap in the perovskite and less photostability under illumination. 31,32 While chlorine substitution might promote the formation of intermediate phases of perovskite, with different optoelectronic properties. 33 Also, the most stabilized in terms of exposure conditions whilst maintaining highly efficient PSCs (PCEs ≥ 23%), have been fabricated by a mixture of different A – cations and different X- anions. By tuning both A – cation and the X – anion, simultaneously, perovskite formulations such as FAₓMA₁₋ₓPbIₓBrₙ⁻ₓ or Csₓ(MA₀.₁₇FA₀.₈₃)₁₋ₓPb(I₀.₈₅Br₀.₁₇)₃, have shown remarkably stability under illumination with PCE ~18 % and at a range of operating conditions for more than 250 hours. 16,34,35

1.3.3 Polytypism in lead iodide (PbI₂)

Lead iodide (PbI₂) is one of the most used inorganic materials towards the synthesis of the photoactive layer in PSCs. It is an intrinsic semiconducting material with wide energy band gap E₉ = 2.3 - 2.4 eV. 36 Its primary crystalline structure is hexagonally close-packed following the space group of P-3m1, consisting of three alternating layers of lead and iodine atoms (I-Pb-I) within the structural unit, which is a near-
octahedron \([\text{PbI}_6]\)^4, as graphically illustrated in figure 1.10. The unit cell dimensions are \(a = b = 0.4557\) nm and \(c = 0.6979\) nm, for the 2H polytypic phase only,\(^{37}\) nonetheless the stacking sequence of the (I-Pb-I), layers can vary significantly, due to the weak van der Waals interactions between those sequential layers, resulting in the complicated crystallochemical phenomenon of polytypism. In which, different polytypes with variable c axis dimensions, which are not independent from the a and b axes, are formed.\(^{38–40}\) Classification between different polytypic phases is made by a number followed by a letter (for example 2H, 4H, 6R), the number corresponds to the repetition and the letter to the type of the crystalline structural unit, respectively. More specifically, the letter "H", in the polytype description indicates the hexagonal unit cell, while ("R") to rhombohedral and ("C") to cubic unit cells, based on the Ramsdell symbols.\(^{41}\) Notable, synthesis of PbI\(_2\) crystallised in cubic structure, has never experimentally or theoretically been recorded.

![Graphical illustration of the alternating layers of lead and iodine atoms (I-Pb-I) within the structural unit of lead iodide (PbI\(_2\)). Black solid spheres are lead atoms and red solid spheres are iodine atoms. \(^{38}\)](image)

Independent of the synthesis process, for example solvothermal,\(^{42}\) co-solvent,\(^{43}\) modified-gel,\(^{44}\) sublimation,\(^{45}\) epitaxial,\(^{46}\) or vertical Bridgman-Stockbarger,\(^{47}\) the formation of multiple polytypic phases present might be responsible for stoichiometric variability and coexistence of several quantum states in PbI\(_2\). While detected reversible and irreversible phase transitions between these polytypic phases,\(^{40,48,49}\) may affect the optoelectronic properties of the PbI\(_2\) and subsequently formed perovskite, in a way that is analogous to polytypism in silicon carbide.\(^{50}\) Despite, the identification of more than 40 polytypic phases of the PbI\(_2\) in the last 60 years, using X-ray diffraction, the
exact mechanism of their formation and diversity, remains unknown. A dominant theory was presented by Frank, attributing the formation of polytypes to crystallographic mismatches during the spiral growth of screw dislocations. Based on that theory, initially PbI₂ platelet shaped structures are formed by surface nucleation and then grow layer-by-layer. These platelets might contain twins, syntactic coalescence or stacking faults originated by the coexistence of more than one polytypic phases, due to thermodynamic fluctuations during the growth process, resulting in sub or over stoichiometric PbI₂. Accordingly, Pandey and Krishna suggested a more complicated approach, based on a faulted basic matrix model to provide a theoretical description of polytypism. Notable that model, considers the three following parameters to have predominant role: i) the energy of the fault near the surface of the matrix during the formation of the screw dislocation, ii) the energy of the screw dislocation and iii) the stacking fault energy of the formatted polytype.

1.3.4 Goldschmidt tolerance factor and beyond

The Goldschmidt tolerance factor was initially introduced by Victor Moritz Goldschmidt in 1926, as a simple dimensionless indicator of crystallographic stability and distortion in oxide perovskites. The stability determined based on the deviation from a close-pack of hard spheres model, based only on the effective ionic radius of the incorporated ions in the general chemical formula of perovskites (ABX₃), and results only a generic expression of the structural stability in perovskites. In the cubic unit cell the edge is equal with two times the length of B-X bond (a = 2d(B-X)), while at the cuboctahedral cage site the width is two times the length of A-X bond (a√2 = 2d(A-X)), combining these two lengths results the equation 1.1.

$$\frac{d_{(A-X)}}{\sqrt{2} \times d_{(B-X)}} = 1$$

Assuming the approximation that the cations and anions in the perovskites with general chemical formula ABX₃ are in contact, the perovskite will crystallize in the ideal cubic structure if the ratio between the ionic radius is equal to unity, as shown in equation 1.2. Where, rₐ, rₖ and rₓ are the radius of A site cation, B site cation and X site anion respectively.
anion, respectively. Values of the tolerance factor can vary from the unity. Theoretical variation of the tolerance factor values are listed in table 1.2.

\[ Tolerance\ factor_{(Goldschmidt)} = \frac{r_A - r_X}{\sqrt{2* (r_B - r_X)}} \approx 1 \]  

\[ \text{equation 1.2} \]

<table>
<thead>
<tr>
<th>Tolerance factor</th>
<th>Structure</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greater than 1</td>
<td>Hexagonal</td>
<td>A cation bigger than B cation or X anion</td>
</tr>
<tr>
<td>From 0.9 to 1</td>
<td>Cubic</td>
<td>Identical ionic radius</td>
</tr>
<tr>
<td>From 0.7 to 0.9</td>
<td>Tetragonal / Orthorhombic</td>
<td>A cation smaller than B cation or X anion</td>
</tr>
</tbody>
</table>

\[ \text{Table 1.2: Range of Goldschmidt’s tolerance factor values and the resulting structure.} \]

However, in the non-oxygen based perovskites the accompanied distortion in the resulting crystal structure is affected by the ionic radius of the incorporated ions, as a function of their centre of mass. Since different organic A-site cations have got more than one degrees of rotational freedom, resulting in an anisotropic molecular Coulomb interaction with respect to the ions present into the perovskite crystal cage, Kieslich et al. have proposed a tolerance factor including an effective radius of the used ions, instead of their ionic radius. The resulting effective ionic radius, includes the size correction in respect to the distance between the farthest atom (excluding hydrogen atoms) from the molecule’s centre of mass. This revised expression of the tolerance factor for perovskites, is shown in equation 1.3. Where \( h_X \text{effective} \) is the effective height in the perovskite unit structure.

\[ Tolerance\ factor_{(Kieslich)} = \frac{r_{A\text{effective}} + r_{X\text{effective}}}{\sqrt{2* (r_B + h_{X\text{effective}})}} \]  

\[ \text{equation 1.3} \]
However, Bartel et al. proposed a new revised tolerance factor based on a novel sure independence screening and sparsifying operating (SISSO) simulation. This new tolerance factor considers the oxidation state of the A site cation towards the stability and compatibility of perovskite structure, as shown in equation 1.4. In a set of 576 simulated perovskite or non-perovskite compounds with general chemical formula ABX$_3$, Bartel’s tolerance factor predicted successfully 92 % of those tested compounds, in contrast with the only 74 % of correct predictions based on the Goldschmidt’s tolerance factor. In which, $n_A$ is the oxidation state of the A site cation, while $r_A$, $r_B$ and $r_X$ are the effective ionic radius of A site cation, B site cation and X site anion, respectively.\(^{56}\)

$$Tolerance \ factor_{(Bartel)} = \frac{r_X}{r_B} - n_A \left( n_A - \frac{r_A/r_B}{\ln(r_A/r_B)} \right) \quad \text{equation 1.4}$$

### 1.3.5 Octahedral factor

In addition to Goldschmidt’s tolerance factor, the octahedral factor ($\mu$) has also been proposed as an extra factor of the perovskites’ structural stability, in consideration of the formatted octahedron cages. The octahedral factor is the ratio between the effective ionic radius of the B site cation, in respect to the X site anion. This dimensionless number indicates how many times the radius of the X site anion fits into the radius of the B site cation, as shown in equation 1.5.\(^{57-59}\)

$$\mu = \frac{r_B}{r_X} \quad \text{equation 1.5}$$

Also, the values for the octahedral factor lies on the range $\sim 0.4 < \mu < \sim 0.7$, as predicted by Rohrer et al. and Li et al. for lead and tin-based hybrid perovskites, respectively.\(^{60}\) Combined values of Goldschmidt’s tolerance and octahedral factors provide
graphically an estimated expression of the relative stability as calculated by Green et al. for lead or tin-based hybrid perovskites, as shown in figure 1.11. 

Figure 1.11: The corresponding combined values of Goldschmidt’s tolerance and octahedral factors for lead or tin based hybrid perovskites, in respect to different A-site cation used (methylammonium (MA+) or ethylammonium (EA+)).61

1.3.6 Solar irradiation

An essential parameter for the efficient operation of photovoltaics fabricated with any device configuration or materials employed, is the solar irradiation. The absorbed flux of photons and their conversion into charge carriers are quantified by many factors leading to photovoltaic devices with maximum efficiency. The solar radiation varies throughout the day and global position, causing inhomogeneous distribution of the flux of photons. Standardized solar reference spectrum is required to allow the performance comparison of fabricated photovoltaic devices either in research laboratories or between manufacturers. That complies with the implementation of the international standard solar radiation spectrum ASTM G-173-03 (ISO 9845-1) in 1992. In addition, the standardization of the solar radiation is defined by three spectra, including the terrestrial and space applications. The AM1.5 global spectrum, is referenced for flat plate photovoltaic modules, having an integrated power of 1000 W
/ m², proportionally similar to the power used for the simulated spectrum in laboratories. While the AM 1.5 direct (plus circumsolar) spectrum is defined for solar concentrator modules with integrated power of 900 W / m². The circumsolar irradiation (or aureole) refers to the sun-light that appears to originate from the region around the sun (a small region which is formed around the sun at angle of ~2.5 degrees in respect to an observer on Earth). Also, for space applications the AM 0 spectrum is used with an integrated power of ~ 1366 W / m², since the absorbance of photons is limited by the absence of air mass. All these three standard solar spectra for terrestrial or space applications are graphically plotted, as shown in figure 1.12. The notation AM at each standard solar irradiation spectrum, is referred to the air mass and quantifies the reduction of the solar power as it passes through the atmosphere and photons absorbed by the air, dust or particle molecules. The mathematical expression for the air mass definition, related to the angle of the incident photons hitting the surface of Earth as function of the maximum position of sun (θ = zenith angle in degrees) is given by the equation 1.6.

Figure 1.12: Standard solar spectra for terrestrial or space applications. Source – NREL (National Renewable Energy Laboratory) (https://www.nrel.gov/grid/solar-resource/spectra.html).
The emergence of perovskite solar cells has undoubtedly motivated both academic and industrial sectors, for research and investment in that specific field of photovoltaics. Since their high-power conversion efficiencies, the materials required and the fabrication techniques that have been employed to manufacture them, reflects a cross mark of low cost and high yield ratio for the next generation of photovoltaic solar cells. The photovoltaic effect in perovskite solar cells, utilizing the perovskite as a photoactive layer for photon harvesting, could be divided into three main operating steps: (1) absorption of photons and conversion into excitons inside the perovskite photoactive thin film, (2) separation of excitons into charge carriers (each exciton is a pair of a negative charged (electron) and a positive charged (hole) carriers) and (3) extraction of those charge carriers. After the exciton dissociation, due to their low binding energy at around ~ 12 meV at room temperature, charge carriers (electrons and holes) are separated and selectively extracted from the perovskite by the electron transporting layer (ETL) and hole transporting layer (HTL), respectively. After drift of charge carriers through the ETL and HTL, their injection and extraction occur into conductive electrodes. Towards the optimization of perovskite solar cells, a range of organic or inorganic ETL and HTL have been used, as shown in figure 1.13. Energy level alignment of those transporting layers within the perovskite’s conduction or valence bands, high charge carrier internal mobilities, chemical / photochemical stability and solvent compatibility, are the main factors of their selection. Also, different conductive electrodes have been used to fabricate the resulting PSCs. Generally, good energy alignment between the HTL or ETL with the work function of the conductive electrodes requires the use of transparent conductive oxide (TCO) on glass or polymeric substrates, such as fluorine doped tin oxide (FTO), indium doped tin oxide (ITO) or aluminium doped zinc oxide (AZO). The criteria of TCO selection includes high conductivity and high optical transparency, in respect to the photoactive thin film. While, aluminium, silver or gold are used as metallic conductive electrodes to achieve the completion of the device enabling it to be connected to an electric circuit.
All these individual layers, that are required to compose the PSCs, could be distinguished into two device fabricating architectures, the regular \((n – i – p)\) or the inverted \((p – i – n)\), as shown in figures 1.14a and 1.14b. 67–69

Figure 1.13: Energy levels (valence band or HOMO) and (conduction band or LUMO) of different materials, acting as electron transporting layer (ETL) and hole transporting layer (HTL).

Figure 1.14: Perovskite device architectures and energy band alignment: (a) regular \((n – i – p)\) and (b) inverted \((p – i – n)\).

These two device architectures can be further divided into two configurations. The mesoscopic or the planar device architectures. The mesoscopic device architecture, characterized by the use of a mesoporous scaffold layer made of titanium dioxide \((\text{TiO}_2)\) or aluminium oxide \((\text{Al}_2\text{O}_3)\) acting as an electron conductive layer or nickel oxide
(NiO) acting as a hole conductive layer, with thicknesses from 150 to 300 nm that is filled with perovskite, while the planar device architecture consisted by a sequence of planar layers, as shown in figure 1.15. However, perovskite solar cells, free of either ETL or HTL, have demonstrated remarkably functional devices. Ke et al. fabricated free of ETL perovskite devices with structure glass / TCO / perovskite / HTL / gold and champion efficiency 14.14 %. While Lin et al. fabricated free of HTL perovskite devices with structure glass / TCO / ETL / perovskite / carbon and champion efficiency 14.5 %.

Figure 1.15: Perovskite device architectures: (a) (n – i – p) mesoscopic, (b) (p – i – n) mesoscopic, (c) (n – i – p) planar (regular) and (d) (p – i – n) planar (inverted).

1.3.8 Type of defects and their effect in perovskite solar cells

Even though fabrication of perovskite thin films, as a photoactive layer in solar cells, have demonstrated a high tolerance to defects, recent research is still showing that formation of deep defects in perovskite, hinder the power conversion efficiency approaching the Schockley – Queisser limit (~ 31 %). These defects can be classified into four main groups in semiconductors: point, line, surface and volume defects, respectively. Specifically, in ionic crystallized materials such as the perovskites, vacancies, interstitials, substitutional, Schottky and Frenkel, consist a sub-group of point defects. While, edge or screw dislocations, make up another sub-group of the line defects. Also, at the sub-group of the surface defects, could be
allocated defects related with twins or grains boundaries. Whereas, voids, cracks, inclusions or precipitates, are collectively known as volume defects, as summarized in table 1.3.

<table>
<thead>
<tr>
<th>Defects in crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Point defects</strong></td>
</tr>
<tr>
<td>Vacancies</td>
</tr>
<tr>
<td>Interstitial</td>
</tr>
<tr>
<td>Substitutional</td>
</tr>
<tr>
<td>Schottky</td>
</tr>
<tr>
<td>Frenkel</td>
</tr>
</tbody>
</table>

*Table 1.3: Classification of defects in crystalline semiconductors.*

Significant scientific research has been published regarding the point and surface defects in perovskites. Specifically, a Schottky point defect occurs when oppositely charged ions (cation and anion) leave their corresponding lattice sites and create a pair of vacancy defects. Also, since that pair of cation / anion leaves the lattice sites simultaneously, the overall electrical neutrality in the crystal is maintained, however the total density of the material is reduced, affecting the material's molecular weight, as shown in figure 1.16 a. Whereas, Frenkel defects consist of a combination of a vacancy and an interstitial point of defect. When an ion leaves its original lattice site, creates a vacancy, that ion occupies an interstitial lattice site, as shown in figure 1.16 b.
It is known that Schottky, Frenkel and grain boundary defects influence in a negative way the device performance of perovskite solar cells. The nature and density of those defects, could have impact in the long-term stability and reproducibility of perovskites as light harvesting layers. Schottky and Frenkel defects, are also responsible for the formation of shallow or deep energy levels, acting as traps of charge carriers, below the conduction band or above the valence band. The number of photo-generated charge carriers within the photoactive layer, is reduced by the opposite process, known as recombination. Generally, in semiconductors and consequently in perovskites, there are two types of recombination, radiative and non-radiative. Any photoexcited electron which exists in the conduction band, is in a meta-stable energy state. If it is not extracted, it will eventually transit into the valence band, which is in a lower energy state. Therefore, when the electron stabilizes back into the valence band, recombining with a hole, emitting a photon with the energy difference between the conduction and valence bands or with the energy difference between any shallow / deep state and valence band, as shown in figure 1.17. On the other hand, non-radiative recombination, are categorized into two major types, the Shockley-Read-Hall (SRH) and Auger. In SRH recombination of charge carriers, the electron is trapped in a normally forbidden energy state (shallow or deep trap level), which has been introduced by defects or a doping agent, while a hole moves up to the same energy.

Figure 1.16: Representation of (a) Schottky and (b) Frenkel point defects in ionic crystals.
state before the electron is thermally re-emitted into the conduction band. The rate between these energy transitions of charge carriers depends on the distance of the introduced forbidden energy states, with respect to the energy band edges (valence and conduction bands). Whereas, Auger recombination involves three charge carriers. The recombination of an electron with a hole, however, instead of emitting the energy as photon or heat, exchanges that energy to a third carrier, an electron or a hole which lives in the conduction or valence bands. After multiple collisions with the crystal lattice, that third carrier relaxes back to the edge of the band. The probability of Auger recombination increases in semiconductors, proportionally to the concentration of doping agents and only under non-equilibrium conditions, for example under illumination in solar cells. Additionally, one of the most prevalent mechanisms of charge carrier losses in perovskites, originates through surface and interface recombination between the boundaries of neighbour grains of perovskite and individual incorporated layers (ETL, HTL, conductive electrodes). Trap centres are formed near the surfaces or interfaces of the perovskite photoactive layer or between neighbour grains, due to dangling bonds (or ions diffusion), caused by the discontinuation of the perovskite in respect to the HTL and ETL layers or crystallization process, respectively.

Figure 1.17: Representation of shallow / deep trap levels and density of charge carriers (electrons / holes) (black curve) into the energy band gap of perovskites.
Previous experimental results have shown that the density of defects and their energy allocation into the energy band gap of perovskites is related to the deposition method or conditions. For example, Nazeeruddin et al. have reported that defects related to iodine anions cause the formation of a shallow electron trap level which lies 0.62 eV below the conduction band using one-step deposition technique. In contrast, when a two-step deposition was used, results in the formation of a deeper electron trap level with energy 0.75 eV below the conduction band. Also, Grätzel et al. have already demonstrated suppression of deep trap levels in the perovskite by adding an excess of lead iodide (Pbl₂). Whereas, Sargent et al., predicted by computational simulations that growth of perovskite under iodine-rich conditions, promotes the formation of deep electron trap levels. In addition to that, stoichiometric variations between the initially organic / inorganic precursors used or inhomogeneous crystallization mechanism of the perovskite growth, results in the formation of point and surface defects at the grain boundaries of the polycrystalline perovskite thin films. Their concentration has already been visualized by Snaith et al. using photoluminescence spectroscopy (PL) measurements. Defect concentrations at the grain boundaries with densities \(10^{16} \text{–} 10^{17} \text{cm}^{-3}\) was confirmed in polycrystalline perovskite thin films, in comparison to the lower values in perovskite single crystals \((10^9 \text{–} 10^{10} \text{cm}^{-3})\). However, many concerns remain about the charge carrier losses through grain boundaries and the overall perovskite device performance, related to the size of individual perovskite grains and unbalanced accumulation of ions between grains during the crystallization process. Recent, suppression of the surface defects allocated in the grain boundaries of perovskites lead the scientists to adopt chemical passivation, using phenethylammonium iodide (PEAI) as an engineering step, leading to reduced concentration of defects on grain boundaries.

1.3.9 Perovskite single crystals

Further investigation of the perovskite intrinsic properties has also been demonstrated by controllable synthesis of perovskite single crystals. This form of high-quality perovskites is accompanied by remarkably low density of defects \(< 10^{10} \text{cm}^{-3}\), long diffusion lengths for the charge carriers \(> 1 \text{mm}\) and chemical stability \(> 10.000\)
hours). These extraordinary long diffusion lengths are derived from the low densities of defects, resulting optimum transportation and extraction of charge carriers within the perovskite material. 85–87 Synthesis of perovskite single crystals with variable organic and halogen moieties has been achieved by different growth processes and summarized in Table 1.4. In 1987, Poglitsch et al. fabricated perovskite single crystals via a solution temperature lowering (STL) growth process, in which the solution of gamma butyrolactone (GBL) / dimethylformamide (DMF) / dimethylsulfoxide (DMSO) and mixed ions was heated to 100 °C followed by cooling down to room temperature. Also, by controlling the cooling rate (0.1 - 0.2 °C * h⁻¹) Su et al. succeeded to fabricate larger in size perovskite single crystals (> 1 cm) by reselecting and regrowing smaller single crystals (seeds). 88,89 Lian et al. prepared centimetre-size perovskite single crystals without using multiple seeds by the bottom seeded solution growth (BSSG) process. 90 Whereas, Tao et al. reported tin-based mixed halogen centimetre-size perovskite single crystals by employing a top seeded solution growth (TSSG) process. 91,92 However, due to the prolonged in time STL growth process (~ 1 – 2 weeks), Saidaminov et al. designed the inverse temperature crystallization (ITC) process, which results synthesis of perovskite single crystals within ~ 3 – 4 hours. Mixed organic / inorganic precursors are dissolved in GBL and the temperature gradually increased (~ 190 °C) until single crystals of perovskite are formed during the ITC growth process. 93,94 Also, fast crystallization growth of single crystals was succeeded by Bakr et al. using the antisolvent vapour assisted crystallization (AVC) process, which is a temperature independent method. Dichloromethane (DCM) was added to the mixture of DMF / GBL and organic / inorganic ions, causing a supersaturated solution promoting single crystal formation. 85 Monocrystalline perovskite thin films were successfully grow by the same group, developing the cavitation triggered asymmetrical crystallization (CTAC) process, in which ultrasonic pulses were introduced into the supersaturated in antisolvent vapor solution, accelerating the formation of homogeneous free of grain boundaries perovskite thin films. 95 Additionally, large area (~ 120 cm²) monocrystalline perovskite thin films with controllable thickness (0.1 – 0.8 mm) were developed by Rao et al. using space limited inverse temperature crystallization (SLITC) process. 96 However, since the high toxicity of DMF and DCM solvents, Acik et al. synthesised perovskite micro-crystals with size < 20 μm at different temperatures and in time duration of 48 hours, using the system of PbI₂ and CH₃NH₃I in a range of non-toxic alcohols. 97
<table>
<thead>
<tr>
<th>Method of growth</th>
<th>Single crystal</th>
<th>Size</th>
<th>Duration of growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution temperature lowering (STL)</td>
<td>CH$_3$NH$_3$PbX$_3$ (X = Cl, Br, I)</td>
<td>~ 5 mm</td>
<td>3 hours (ref. 87)</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$PbX$_3$ (X = Br, I)</td>
<td>&gt;10 mm</td>
<td>240 hours (ref. 88)</td>
</tr>
<tr>
<td>Bottom seeded solution growth (BSSG)</td>
<td>CH$_3$NH$_3$PbI$_3$</td>
<td>&gt;12 mm</td>
<td>360 hours (ref. 89)</td>
</tr>
<tr>
<td>Top seeded solution growth (TSSG)</td>
<td>CH$_3$NH$_3$SnI$_3$</td>
<td>~ 10 mm</td>
<td>Not provided (ref. 90)</td>
</tr>
<tr>
<td></td>
<td>CH(NH$_2$)$_2$SnI$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inverse temperature crystallization (ITC)</td>
<td>CH$_3$NH$_3$PbX$_3$ (X = Br, I)</td>
<td>~ 5 mm</td>
<td>~ 3 - 4 hours (ref. 92)</td>
</tr>
<tr>
<td>Antisolvent vapor assisted crystallization (AVC)</td>
<td>CH$_3$NH$_3$PbX$_3$ (X = Br, I)</td>
<td>&gt;10 mm</td>
<td>Not provided (ref. 84)</td>
</tr>
<tr>
<td></td>
<td>CH$_3$NH$_3$PbBr$_3$</td>
<td>2 mm x 2 mm x 0.005 mm</td>
<td>~ 3 - 6 hours (ref. 94)</td>
</tr>
<tr>
<td>Cavitation triggered asymmetrical crystallization (CTAC)</td>
<td>CH$_3$NH$_3$PbBr$_3$</td>
<td>180 mm x 67 mm x 0.4 mm</td>
<td>~ 170 hours (ref. 95)</td>
</tr>
<tr>
<td>Space limited inverse temperature crystallization (SLITC)</td>
<td>CH$_3$NH$_3$PbBr$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohol</td>
<td>CH$_3$NH$_3$PbI$_3$</td>
<td>&lt; 20 μm</td>
<td>48 hours (ref. 96)</td>
</tr>
</tbody>
</table>

Table 1.4: Perovskite single crystals or monocrystalline thin films growth processes.
Also, due to the superior quality of perovskite single crystals, many groups have used alternative solid-state methods of perovskite synthesis, resulting in controllable stoichiometry. Grätzel et al. and Biswas et al. have synthesized CH$_3$NH$_3$PbI$_3$ and CsPbBr$_3$ powders, respectively, by using a mortar as a solvent free mechanochemical way.\textsuperscript{98,99} While, Manukyan et al. have synthesized CH$_3$NH$_3$PbI$_3$ powder by employing a ball milling process.\textsuperscript{100} Notable, synthesis of perovskite oxide powders with high yield and purity by using a planetary ball milling method, has been realized by Lee et al. and Zhang et al.\textsuperscript{101,102}

1.3.10 Optoelectronic properties: from p-n junction to perovskites

A pure semiconducting material such as, silicon or germanium, is characterized intrinsic or undoped, when not dopant species of other materials are present. The concentrations between charge carriers (electrons and holes) in intrinsic semiconductors are equal, resulting in a minimum of electrical conductivity. However, to improve the electrical conductivity among many other parameters, different dopant elements are used. The material and amounts of doping elements define the type of doped semiconductor. N-type silicon semiconductors are synthesized by doping the intrinsic one with an electron donor element, such as phosphorous or arsenic. The term n-type points out that the majority of charge carriers are electrons, while holes are the minority carriers. In contrast, p-type silicon semiconductors are synthesized by doping the intrinsic one with an electron acceptor element, such as boron or gallium. Again, the term p-type indicates that the majority of charge carriers are holes, whereas electrons are the minority carriers. Variability between charge carrier concentrations results in variable electrical conductivity in semiconductors and can be represented by the Fermi level ($E_F$) within the energy band gap ($E_g$). In n-type semiconductors the Fermi level is closer to the conduction band (CB), while in p-type semiconductors the Fermi level is closer to the valence band (VB), respectively, as shown in figure 1.18.
Figure 1.18: Energy levels (valence band (VB), conduction band (CB) and Fermi level (E_F)) in (a) intrinsic, (b) n-type and (c) p-type semiconductors. White circles represent positive charge carries (holes), whereas red circles represent negative charge carriers (electrons).

The combined junction between p-type and n-type semiconductors allows electrical current to pass only in one direction into the junction, known as a diode. Also, the resulting p-n heterojunction is the interface between two semiconducting layers of dissimilar crystalline structures and with different energy band gaps (belonging to the III-IV family of doped semiconductors), in comparison with a p-n homojunction, in which the formatted diode based on the different doping of regions inside the same intrinsic semiconducting material. Notably, in p-n heterojunction semiconductors, the formatted energy discontinuity (formation of quantum well) as a function of the individual energy band gap of the incorporated p and n type semiconductors, resulted from the difference between the energy band gaps of p and n types semiconductors and the crystal structure dissimilarity at their interface, as schematically represented in figure 1.19. Depending on the concentration of the dopant agents in both p-type and n-type semiconductors in a p-n junction, diffusion of free (in majority) electrons from the n-type side into the p-type side, results the diffusion current. While free in minority electrons from the p-type side drift into the n-type side at the same time, results the drift current. This gradient of free charge carriers flow, creates an electric field as function of the distance (E(x)) near the p-n junction interface, since both positively charged (donor) dopant ions in the n-type side and negatively charged (acceptor) dopant ions in the p-type side are immobile. Leading to the n-type side to become positively charged, while the p-type side to become negatively charged.
These combined regions, form a depletion region for mobile charge carriers through the electric field. The Fermi level in a p-n junction under thermal equilibrium remains at equal stable energy level, leading to the formation of a contact potential $qV_0$. The total density of current flow for both n-type side and p-type side due to drift of charge carriers into the electric field and the diffusion of charge carriers by the concentration gradient is equal to zero, as shown in figure 1.20.  

---

**Figure 1.19**: Basic schematic representation of p-n homo and hetero junctions. (a), (c) and (e) in thermal equilibrium, whereas (b), (d) and (f) in contact, respectively. Blue lines represent valence bands, while red lines represent conduction bands, dashed lines represent Fermi energy levels.  

---

**Figure 1.20**: (a) Depletion region formation and (b) energy diagram and band bending over the depletion region for a p-n homojunction.
The potential in the depletion region can be calculated by assuming that an instant transition between the depleted of charge carriers and non-depleted in the p and n regions. The charge densities in the depletion region for the p and n sides are $\rho_p = -eN_A$ and $\rho_n = +eN_D$, where $N_A$ and $N_D$ are the concentrations of acceptors and donors, respectively. Since, the total charge is neutral at the depletion region as expressed by the equation $N_A * d_p = N_D * d_n$, where $d_p$ and $d_n$ are the depths of the depletion region for both the p and n type sides, the potential can be calculated by solving the Poisson’s equation (equation 1.7), in which $\rho$ is the charge density distribution, $\epsilon$ is the dielectric constant of the semiconductor and regarding the conditions that the gradient of the potential at the boundaries ($x = -d_p$ and $x = d_n$) is equal to zero.

$$\frac{d^2U(x)}{dx^2} = -\frac{\rho}{\epsilon \epsilon_o} \quad \text{(equation 1.7)}$$

The total difference of the potential across the depletion region based on the equation 1.7 is:

$$\Delta U = \frac{\epsilon}{2\epsilon \epsilon_o} \left(N_D d_n^2 + N_A d_p^2\right) \quad \text{(equation 1.8)}$$

Also, based on the charge neutrality conditions into the depletion region, the calculated widths for both the p and n type sides are:

$$d_p = \sqrt{\left(\frac{\Delta U 2 \epsilon \epsilon_o}{e N_A} \frac{N_D}{N_A + N_D}\right)} \quad , \quad d_n = \sqrt{\left(\frac{\Delta U 2 \epsilon \epsilon_o}{e N_D} \frac{N_A}{N_A + N_D}\right)} \quad \text{(equation 1.9)}$$

In addition, regarding the Boltzmann approximation for the densities of carriers (majority and minority) into the p and n type sides, these can be written:

$$n_p = N_c ef \frac{\left(E_F - E_g - e \Delta U\right)}{k_B T}, \quad p_p = N_c ef \frac{\left(-E_F - e \Delta U\right)}{k_B T} \quad \text{(equation 2.0)}$$

$$n_n = N_c ef \frac{\left(E_F - E_g\right)}{k_B T}, \quad p_n = N_c ef \frac{\left(-E_F\right)}{k_B T} \quad \text{(equation 2.1)}$$
In those equations, \( n_n \) and \( p_n \) are the electron and hole densities in the n-type side, while \( n_p \) and \( p_p \) are the electron and hole densities in the p-type side. Also \( N_{\text{eff}}^C \) and \( N_{\text{eff}}^V \) are the effective density of states in the conduction and valence bands, respectively. Without any applied external voltage across the p-n homojunction, the drift and diffusion currents are proportionally equal in both p-type and n-type sides and can be written:

\[
|I_{\text{diffusion}}| = |I_{\text{drift}}| = |I_0| = Ce \left( \frac{E_F - E_g - \epsilon \Delta U}{k_B T} \right) \quad \text{(equation 2.2)}
\]

Where \( I_0 \) called reverse saturation current with values \( \sim 100 \) nA, while \( C \) is a constant regarding the elementary charge \( (q) \) and area between p-n junction interface, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. If an external positive voltage is applied across the p-n homojunction (n-type side negatively charged and p-type side positively charged), the electron drift current remains unchanged, while the diffusion current is modified because the chemical potential on the n-type side is shifted by \( + eV \) and the total current in that forward bias condition is:

\[
I = |I_{\text{diffusion}}| - |I_{\text{drift}}| = Ce \left( \frac{E_F + eV - E_g - \epsilon \Delta U}{k_B T} \right) - Ce \left( \frac{E_F - E_g - \epsilon \Delta U}{k_B T} \right) = I_0 \left( e^{eV/k_B T} - 1 \right) \quad \text{(equation 2.3)}
\]

Whereas, if an external negative voltage is applied across the p-n homojunction (n-type side positively charged and p-type side negatively charged), the electron drift current remains unchanged, while the diffusion current is modified because the chemical potential on the n-type side is shifted by \( - eV \) and the total current in that reversed bias condition is:

\[
I = |I_{\text{diffusion}}| - |I_{\text{drift}}| = Ce \left( \frac{E_F - eV - E_g - \epsilon \Delta U}{k_B T} \right) - Ce \left( \frac{E_F - E_g - \epsilon \Delta U}{k_B T} \right) = I_0 \left( e^{-eV/k_B T} - 1 \right) \quad \text{(equation 2.4)}
\]

The relative motion (diffusion or drift) of majority and minority charge carriers between the interfaces in a p-n homojunction, when either thermal equilibrium or forward or reverse bias is applied illustrated in figure 1.21.
During the electrical characterization of a p-n junction, the relation between the total current and voltage either under illumination or at dark conditions, is expressed by the equation 2.5, in which \( n \) is the ideal factor with values at the range \( 1 < n < 2 \). Deviation of the ideal factor from the unity indicates formation of a non-ideal diode, resulting increased concentration of recombination centers either in the photoactive layer or between transporting layers and selective contacts.\(^{108,109}\)

\[
I_{\text{total}} = I_0 \left( e^{\frac{eV}{n k_B T}} - 1 \right) - I_{\text{photocurrent}} \quad \text{(equation 2.5)}
\]

The characteristic current – voltage curve (I-V) of a diode is vertically lowered proportionally to the photocurrent produced at the 4\(^{th}\) quadrant under illumination, enabling the extraction of power from solar cells, as shown in figure 1.22. Under short circuit condition, the total current is equal to the photocurrent, while under open circuit condition the total current is zero and the voltage is:

\[
V_{oc} = \frac{n k_B T}{e} \ln \left( \frac{I_{\text{photocurrent}}}{I_o} + 1 \right) \quad \text{(equation 2.6)}
\]

The open circuit voltage is increased proportionally to the flux of incident photons, however its highest value is limited by the p-n junction properties and operating temperatures. Also, the maximum current and voltage corresponding to the maximum power point (MPP), is related with the squareness of the I-V curve in the 4\(^{th}\) quadrant and expressed by the fill factor (FF), as shown in figure 1.23 a. Highest values of FF
indicate better operating performance of solar cells and is affected by the series resistance ($R_{\text{series}}$), which is related with losses in the photoactive layer, conductivity, interfaces and energy alignment with respect to the incorporated layers and the shunt resistance ($R_{\text{shunt}}$), which is related with the losses introduced by shunt paths or pinholes present in the photoactive thin film, as shown in figure 1.23 b. An ideal solar cell should have lower values of $R_{\text{series}}$ and higher $R_{\text{shunt}}$, as well. The percentage of power conversion efficiency (PCE), is calculated based on equation 2.7, in respect to the power of incident photons (1000 W / m$^2$ = 1 sun).

$$PCE\% = \frac{P_{\text{output}}}{P_{\text{input}}} = I_{\text{MPP}}*V_{\text{MPP}} = \frac{FF*V_{\text{oc}}*I_{\text{sc}}}{1000 W/m^2} \quad \text{(equation 2.7)}$$

![Figure 1.22: Characteristic current – voltage curve of a p-n homojunction at dark condition (dashed curve) or under illumination (solid curve).](image)
Figure 1.23: (a) Illustration of the maximum power point (MPP), fill factor (FF), short circuit current ($I_{SC}$) and open circuit voltage ($V_{OC}$), (b) the effect of series resistance ($R_{series}$) and shunt resistance ($R_{shunt}$), in a characteristic current – voltage curve of a p-n homojunction.
However, significant current and voltage losses in solar cells related to five different mechanisms, resulting reduced values of PCE, in respect to the maximum Shockley-Queiseer limit, which is about 31 % for PSCs (using a single photoactive layer). Mismatch between the absorption of photons with energy equal to the perovskite photoactive layer \( E_g \) and the wide energy of photons of the solar spectrum, results in the non-absorption of photons with energy below the \( E_g \). Also, strong interactions between the photo-excited charge carriers and lattice phonons introduce thermalization losses, reducing the open circuit voltage. While losses related to Kirchoff’s law, are responsible for emission losses, since photoactive layers behave as absorbers and emitters simultaneously. In addition to that, during the absorption and emission of photons from the photoactive layer in an anisotropic way (multiple angles), results an increase in entropy due to the expansion of photon modes, known as Boltzmann losses. Finally, temperature difference between the ambient and solar cell during its operation cause thermodynamic Carnot losses. All these combined losses originated by these five difference mechanisms, are mainly considered to reduce by almost ~ 69 % the maximum conversion of photons to charge carriers, as function of the perovskite photoactive layer \( E_g \) and in respect to the power of incident flux of photons (1000 W/m\(^2\) = 1 sun), as summarized in table 1.5 and graphically illustrated in figure 1.24.\(^{110,111}\)

<table>
<thead>
<tr>
<th>Mechanism of PCE reduction</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below ( E_g )</td>
<td>25.5</td>
</tr>
<tr>
<td>Thermalization</td>
<td>30.5</td>
</tr>
<tr>
<td>Emission</td>
<td>1</td>
</tr>
<tr>
<td>Carnot</td>
<td>2.5</td>
</tr>
<tr>
<td>Boltzmann</td>
<td>9.5</td>
</tr>
<tr>
<td><strong>Shockley-Queiseer limit</strong></td>
<td><strong>31</strong></td>
</tr>
</tbody>
</table>

Table 1.5: Percentage of losses based on the five different mechanisms and Shockley-Queiseer limit in PSCs (numerical values are referred based on simulated models).\(^{111}\)
Figure 1.24: Graphically illustration of intrinsic loss mechanisms in single photoactive layer with variable $E_g$ as function of the incident photons radiation, leading to reduced PCE. $^{111}$

Also, the equivalent electrical circuit of a typical solar cell fabricated based on the silicon p-n homojunction, excluding any external resistors of additional metallic contacts, consisted by one diode, the shunt resistance and the series resistance, as depicted in figure 1.25 a. Whereas, the equivalent electrical circuit of a typical solar cell fabricated based on the perovskite either p-i-n or n-i-p heterojunction, excluding any external resistors of additional metallic or TCO contacts, consisted of two diodes, the shunt resistance and the series resistance, as suggested by Liao et al. and shown in figure 1.25 b. $^{112}$
Figure 1.25: Illustration of the equivalent electrical circuits for solar cells based on (a) silicon single p-n homojunction and (b) perovskite either p-i-n or n-i-p heterojunction.

1.3.11 Current-voltage hysteresis

One of the main problems during the electrical characterization of PSCs, is the hysteresis phenomenon, with an observable offset between the characteristic current – voltage curves in respect to the forward and reverse scan directions (forward: from \( I_{SC} \) to \( V_{OC} \), reverse: from \( V_{OC} \) to \( I_{SC} \)) and significantly affected by the scan speed. This hysteretic behaviour has been explained by several mechanisms and depends on ionic motion, localized current fluctuations due to depolarization of ionic accumulation at the interfaces between the HTL / perovskite and perovskite / ETL and at grain boundaries. \(^{113-115}\) This hysteresis trend is also described by two models. The first model considers the formation of an electric field through the device which is different from the work functions between the two contacts (TCO and metal). This electric field affects the motion of charge carriers in respect to the transporting layers and modified
by the magnitude and speed of the external applied voltage during the electrical characterization. The mobile free ions can drift along the electric field inside the photoactive material, forming two space charge layers that shield or screen the main net electric field between the perovskite / ETL and perovskite / HTL. The formation of those space charge layers influence the charge carrier's collection as shown by step-dwell probe and step-dwell-step probe measurements conducted by Calado et al. and Belisle et al., respectively. The second model regards the influence of interfacial chemical reactions between the perovskite / ETL and perovskite / HTL layers. Low or high frequency capacitance measurements in PSCs under illumination, have revealed different degree of interaction between the perovskite with compact titanium dioxide (c-TiO$_2$), phenyl-C61-butyric acid methyl ester (PC$_{61}$BM), nickel oxide (NiO) or 2,2',7,7'-tetakis [$N,N$-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-MeOTAD). The formation of weak Ti – I – Pb bonds, accompanied by reversible accumulation of iodine ions causing enhanced hysteresis, in comparison with PC$_{61}$BM as an ETL layer used.

1.4 Aims for the thesis

Organic-inorganic halide perovskite semiconductors have attracted considerable academic and industrial attention in the last decade, since they have shown comparable or superior optoelectronic properties in comparison with other relevant semiconducting materials (such as silicon, CIGS, CZTS, CdTe, GaAs). Also, their low-cost fabrication applicability into solar cells, light emitting diodes (LED), photodetectors and even batteries have driven research efforts for their further exploitation and materials’ quality optimization. However, halide perovskite commercialization perspective is hindered by lead (Pb) toxicity, chemical instability, large scale reproducibility and materials purity.

In this thesis, the first aim was to understand the importance of stoichiometry and polytypism in PbI$_2$ used, toward the synthesis of the simplest hybrid perovskite CH$_3$NH$_3$PbI$_3$ as a photoactive material in PSC devices. To study these two properties (stoichiometry and polytypism) of PbI$_2$, two different routed of synthesis were selected. Planetary ball milling (water-free) and the solvothermal (present of water) processes
were selected to investigate whether it is possible to control the stoichiometry and polytypic phases present in PbI₂. The presence of polytypic phases and the stoichiometry of the synthesized PbI₂ were confirmed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Rutherford backscattering spectroscopy (RBS), as discussed in chapter 3.

The second aim was to correlate the PCE of PSC devices with the stoichiometry and polytypic phases present in the PbI₂ used. To study that a stoichiometrically optimum PbI₂ synthesized by planetary ball milling was compared with commercially available PbI₂. Also, as experimentally shown, the PCE of PSC devices was affected by the stoichiometry and not the number of polytypes present in PbI₂. That was directly related with the atomic ratio between the lead and iodide, as confirmed by controllably synthesis of CH₃NH₃PbI₃ micro-crystals. Whereas, when sub-stoichiometric PbI₂ used for the formation of CH₃NH₃PbI₃, resulted in unreacted PbI₂, as evidenced by ultra-violent visible spectroscopy (UV-Vis), which affects the average PCE of PSC devices by a factor of ~ 3.3 times. Unreacted PbI₂ might be correlated to further chemical instability in CH₃NH₃PbI₃, as discussed in chapter 3.

The third aim was to understand the chemical instability and correlate the phenomenon of hysteresis between the characteristic current density-voltage curves at forward and reverse scans in PSC devices, as function of mixed organic cations and halogen anions introduced into the CH₃NH₃PbI₃ crystal structure. That succeeded by synthesizing controllably doped CH₃NH₃PbI₃ micro-crystals and tracing the optimum amount of dopants used by XRD. Also, stability tests were performed in PSC devices for 240 hours, fabricated using doped CH₃NH₃PbI₃ micro-crystals, as presented in chapter 4.

1.5 References


8 V. V. M. Goldschmidt, *Naturwissenschaften*, 1926, **14 (21)**, 477–485.


Chapter 2

Experimental methods

2.1 Introduction

This chapter describes in detail all the experimental methods used for the synthesis of PbI₂, relevant materials used for fabrication of perovskite micro-crystals, perovskite thin films and perovskite solar cells. Specifically, attention is given to the topic of PbI₂ synthesis by two different processes (solvothermal and mechanochemical) and fabrication of doped / undoped perovskite micro-crystals. Controllable and reproducible synthesis of perovskites is an important step towards the commercialization of perovskite-based solar cell devices. Also, the mechanochemical synthesis of PbI₂ might be applied in lead free precursors (such as tin iodide (SnI₂) or bismuth iodide (BiI₃)) leading to formation of perovskites with less toxicity. Chemicals and reagents, were purchased and used without any further purification, unless is specified. Also, in this chapter information and relevant theory is provided about the characterization techniques used. Characterization of all synthesized materials was conducted at less than 24 hours after their preparation.
2.2 Synthesis of chemicals

2.2.1 Synthesis of organohalide compounds

Generally, organic–inorganic perovskite compounds obeying to the general chemical formula ABX₃, are synthesized by the equimolar reaction between organic halide such as methylammonium iodide (CH₃NH₃I) and inorganic halide such as lead iodide (PbI₂) compounds, as shown in chemical reaction 2.1. However, synthesis of perovskite could result from the reaction between non-equimolar amounts of precursors, such as CH₃NH₃I and lead chloride (PbCl₂), as shown in chemical reaction 2.2, as summarized in table 2.1. That indicates the complexity of perovskites’ synthesis, as a function of their reactant precursors and halogen type. However, this thesis focuses only on the equimolar reactions of reactant compounds (as shown in chemical reaction 2.1) toward the formation of perovskites. Two different amino halogen compounds, CH₃NH₃I and the methylammonium bromide (CH₃NH₃Br) were synthesized by reacting methylamine (CH₃NH₂) with hydroiodic acid (HI) or hydrobromic acid (HBr), respectively, as shown in chemical reactions 2.3 and 2.4. Also, one amidine halogen compound, formamidinium iodide (CH(NH₂)₂I) was also synthesized by reacting formamidine acetate (HN=CHNH₂CH₃COOH) with hydroiodic acid, as shown in chemical reaction 2.5 and summarized in table 2.2.

\[
\text{CH}_3\text{NH}_3\text{I} + \text{PbI}_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3 \quad \text{chemical reaction 2.1}
\]
\[
3 \text{CH}_3\text{NH}_3\text{I} + \text{PbCl}_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x + \text{PbI}_{2-y}\text{Cl}_y \quad \text{chemical reaction 2.2}
\]

Table 2.1: Chemical reactions between organic and inorganic halide compounds towards the formation of perovskite, (2.1) equimolar and (2.2) non-equimolar.

\[
\text{CH}_3\text{NH}_2 + \text{HI} \rightarrow \text{CH}_3\text{NH}_3\text{I} \quad \text{chemical reaction 2.3}
\]
\[
\text{CH}_3\text{NH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{NH}_3\text{Br} \quad \text{chemical reaction 2.4}
\]
\[
\text{HN = CHNH}_2 \cdot \text{CH}_3\text{COOH} + \text{HI} \rightarrow \text{CH(NH}_2)_2\text{I} + \text{CH}_3\text{COOH} \quad \text{chemical reaction 2.5}
\]

Table 2.2: Chemical reactions between amines or amidine and halide acids, (2.3) methylamine with hydroiodic acid, (2.4) methylamine with hydrobromic acid and (2.5) formamidine acetate with hydroiodic acid.
Methylammonium iodide (CH$_3$NH$_3$I) was synthesised in a similar way to Kamat et al.$^2$ by adding 38 mL of hydroiodic acid dropwise (57% w / w in water, Alfa Aesar) into 30 mL of methylamine solution (40% w / w in water, Sigma Aldrich) in a 250 mL round bottom flask at 0 °C (ice bath) and constantly stirring (400 rpm) for 2 hours. After mixing both liquids, the round bottom flask was transferred into an oil bath at a temperature of 90 °C, to evaporate the water for 6 - 7 hours. The resulting yellow/white precipitate was further purified by recrystallisation two times using pure anhydrous ethanol. The white / transparent crystallised flakes were collected by vacuum filtration using a Whatman filter paper grade 5 with a pore size of 2.5 μm and dried in a vacuum oven at 50 °C for 24 hours, before storage in a vial under dark conditions. The same CH$_3$NH$_3$I, was used for both the synthesis of the undoped or doped CH$_3$NH$_3$PbI$_3$ micro-crystals and perovskite solutions, as well.

Methylammonium bromide (CH$_3$NH$_3$Br) was similarly synthesised in a way that presented by Noh et al.$^3$ by adding 43 mL of hydrobromic acid dropwise (48% w / w in water, Sigma Aldrich) into 30 mL of methylamine solution (40% w / w in water, Sigma Aldrich) in a 250 mL round bottom flask at 0 °C (ice bath) and constantly stirring (400 rpm) for 2 hours. After mixing both liquids, the round bottom flask was transferred into an oil bath at a temperature of 90 °C, to evaporate the water for 6 - 7 hours. The resulting yellow/white precipitate was further purified by recrystallisation process two times, using pure anhydrous ethanol. The white / transparent crystallised flakes were collected by vacuum filtration using a Whatman filter paper grade 5 with a pore size of 2.5 μm and dried in a vacuum oven at 50 °C for 24 hours, before storage in a vial under dark conditions. The CH$_3$NH$_3$Br, was used for controllable doping during the synthesis of doped CH$_3$NH$_3$PbI$_3$ micro-crystals.

Formamidinium iodide (CH(NH$_2$)$_2$I) was synthesised in a similar way to Eperon et al.$^4$ by dissolving 8 g of formamidinium acetate powder (99%, Alfa Aesar) in a 1.2 times molar excess of 12.2 mL hydroiodic acid (57% w / w in water, Alfa Aesar) in a 250 mL round bottom flask at 0 °C (ice bath) and constantly stirring (400 rpm) for 2 hours. After mixing both reactants, the round bottom flask was transferred into an oil bath at a temperature of 90 °C, to evaporate the water for 4 - 5 hours. The resulting yellow/white precipitate was further purified by recrystallisation one time using pure anhydrous
ethanol. The white / transparent crystallised flakes were collected by vacuum filtration using a Whatman filter paper grade 5 with a pore size of 2.5 μm and dried in a vacuum oven at 50 °C for 24 hours, before storage in a vial under dark conditions. The CH(NH₂)₂I, was used as controllable doping agent during the synthesis of doped CH₃NH₃PbI₃ micro-crystals.

2.2.2 Synthesis of solvothermal PbI₂

Solvothermal synthesis of PbI₂ powder was achieved by dissolving 1 g of lead (II) nitrate (Pb(NO₃)₂) (≥ 99 %, Sigma Aldrich) and 1.01 g of potassium iodide (KI) (≥ 99 %, Honeyell Fluka) in a 1 L volume round bottom flask filled with 1 L of boiled (100 °C) ultra-pure deionised water (Sigma Aldrich) with resistivity 18.2 MΩ. The round bottom flask was covered with blanket made of fiberglass and left to cool down slowly to room temperature for 24 hours. An excess of potassium iodide moles (~ 2 %) were used to complete the reaction of the Pb(NO₃)₂, as shown in the chemical reaction 2.6. The golden coloured crystalline flakes of PbI₂ (as shown in figure 2.1), were collected after vacuum filtration using Whatman filter paper grade 5 with a pore size of 2.5 μm and dried in a vacuum oven at 50 °C for 24 hours, before storage in a vial under dark conditions.

\[
Pb(NO_3)_2 + 2KI \rightarrow PbI_2 + 2KNO_3 \quad \text{chemical reaction 2.6}
\]

Figure 2.1: Image of solvothermal synthesised PbI₂ powder, scale bar represents 2 cm.
2.2.3 Synthesis of mechanochemical PbI₂

Mechanochemical synthesis of PbI₂ powder was achieved using a planetary ball milling machine (PM 100 Retsch) at variable revolutions per minute and time duration, as shown in table 2.3. Initially, 30 g of Pb(NO₃)₂ (≥ 99 %, Sigma Aldrich), 30.07 g of KI (≥ 99 %, Honeyell Fluka) and 160 stainless steel spheres of diameter 6 mm, were mixed together in a ball milling jar of capacity 500 mL. The yellow coloured PbI₂ powder (as shown in figure 2.2) was then separated from the stainless-steel spheres and washed 5 times with deionised water (70 - 80 mL each time) during vacuum filtration using Whatman filter paper grade 5 with a pore of size 2.5 μm to remove any potassium nitrate by-product. Finally, the PbI₂ was dried in a vacuum oven at 50 °C for 24 hours, before storage in a vial under dark conditions. The yield of the PbI₂ produced was defined by the relative number of moles of product (PbI₂) to the moles of reactant (Pb(NO₃)₂), considering as ideal molecular weight for the PbI₂, to be 461.01 g / mol), resulting:

\[
\left(\frac{40.32 \, g}{461.01 \, g * mol^{-1}}\right) / \left(\frac{30 \, g}{331.21 \, g * mol^{-1}}\right) \times 100 \% \approx 96.5 \%
\]

<table>
<thead>
<tr>
<th>Lead iodide sample</th>
<th>Mechanochemical conditions of synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC1</td>
<td>200 rpm 2 hours</td>
</tr>
<tr>
<td>MC2</td>
<td>400 rpm 1 hour</td>
</tr>
<tr>
<td>MC3</td>
<td>400 rpm 4 hours</td>
</tr>
</tbody>
</table>

*Table 2.3: Mechanochemical PbI₂ powders (MC 1 to 3) synthesized using planetary ball milling process under different conditions (revolutions per minute and time duration).*
2.2.4 Synthesis of undoped or doped CH$_3$NH$_3$PbI$_3$ micro-crystals

Synthesis of undoped or doped CH$_3$NH$_3$PbI$_3$ micro-crystals was achieved based on a method similar to the reaction between alcohol / PbI$_2$ / CH$_3$NH$_3$I, introduced by Acik et al.  

The undoped CH$_3$NH$_3$PbI$_3$ micro-crystals were synthesised by reacting 0.7 g of mechanochemical MC2 or commercial (99.999 %, Sigma Aldrich) PbI$_2$ powder with either an equimolar amount of CH$_3$NH$_3$I (0.2414 g) or an equimolar amount plus 30% excess by weight of CH$_3$NH$_3$I (0.2414 g + 0.0724 g = 0.3138 g), in 15 mL of 1-pentanol at variable temperatures (20 °C, 50 °C, 70 °C and 90 °C) and constant stirring (400 rpm) for 24 hours. In this process, 1-pentanol which is a polar protic non-toxic alcohol, was used to selectively dissolve only the CH$_3$NH$_3$I, but neither the PbI$_2$ powder nor the final product of the undoped CH$_3$NH$_3$PbI$_3$ micro-crystals. The synthesised black powder (as shown in figure 2.3) was collected by vacuum filtration using Whatman filter paper grade 5 with a pore size of 2.5 μm and washed with 5 mL of chlorobenzene
(99.9 %, Alfa Aesar) during the filtration step, followed by drying in a vacuum oven for 30 min at room temperature, before storage in a vial under dark conditions.

Doped CH$_3$NH$_3$PbI$_3$ micro-crystals were synthesised by reacting 0.7 g of mechanochemical MC2 PbI$_2$ powder with an equimolar amount plus 10% excess by weight of CH$_3$NH$_3$I (0.2414 g + 0.0241 g = 0.2655 g) and various amounts (as function of PbI$_2$ moles) of CH$_3$NH$_3$Br, CH(NH$_2$)$_2$I or Br$_2$, respectively. All the mixed precursors were stirred constantly (400 rpm) in 15 mL of 1-pentanol at constant temperature of 90 ºC for 24 hours. The resulting black powder was collected by vacuum filtration using Whatman filter paper grade 5 with a pore size of 2.5 μm and washed with 5 mL of chlorobenzene (99.9 %, Alfa Aesar) during the filtration step, followed by drying in a vacuum oven for 30 min at room temperature, before storage in a vial under dark conditions.

Figure 2.3: Black powder of undoped or doped CH$_3$NH$_3$PbI$_3$ micro-crystals after 24 hours of synthesis in oil bath, scale bar represents 30 mm.
2.3 Preparation of perovskite solutions

2.3.1 Dry dimethyl sulfoxide (DMSO)

Dry dimethyl sulfoxide (DMSO) (≥99.5%, Sigma Aldrich) was prepared by mixing 150 mL of DMSO and 20 g of magnesium sulfate (MgSO₄) (Fisher Chemical) in a 250 mL round bottom flask. The round bottom flask was capped and left in a fume hood at room temperature for at least two weeks before extracting dry DMSO as a transparent colourless solution. The less expensive drying process of DMSO with MgSO₄ was selected in comparison with other processes involving distillation under vacuum or use of molecular sieves.

2.3.2 Perovskite solution preparation for solar cell devices

Two groups of perovskite solutions for the fabrication of solar cell devices were prepared. For the first group, 0.4 g of mechanochemical MC 2 or commercial PbI₂ powders, directly mixed with an equimolar amount of CH₃NH₃I (0.1379 g) and dissolved in 0.620 mL of dry DMSO, with a final concentration of 2.8 M. Whereas, for the second group, 0.4 g of the undoped CH₃NH₃PbI₃ micro-crystals synthesised using mechanochemical MC 2 or commercial PbI₂ powders, dissolved in 0.571 mL of dry DMSO with a final concentration of 1.13 M. All perovskite solutions were kept (capped in the glass vial) on a hot plate at a temperature of 100 °C for 10 min to ensure complete dissolution of the reactants in dry DMSO. Yellowish solutions were filtered through a PTFE filter with a pore size of 0.45 μm into a new clean glass vial and kept under constant stirring (~300 rpm) and temperature (65 - 70 °C) in a custom-made aluminium block before deposition, as shown in figure 2.4. The block helped to reduce condensation of the dry DMSO on the inside walls of the vial and preventing premature perovskite crystallisation. In all the experiments with undoped or doped CH₃NH₃PbI₃ micro-crystals, the solutions were prepared directly after the synthesis of micro-crystals. Also, the volume of dry DMSO added into the undoped or doped CH₃NH₃PbI₃ micro-crystals results in the pre-defined concentration of solutions 1.13 M, calculated based on the assumption of perfectly crystallised micro-crystals with corresponding molecular weights, as defined by the sum of the atomic mass units of each element.
and summarised in table 2.4. Whereas, in all the experiments with either commercial or mechanochemical PbI$_2$ powders, the solution concentrations were calculated based on the false assumption of stoichiometrically perfect PbI$_2$ (Pb : I = 1 : 2, atoms ratio), with molecular weight 461.01 g * mol$^{-1}$.

Figure 2.4: Image of the custom-made aluminium block used to keep the perovskite solutions warm, under constant stirring (~ 300 rpm) at a temperature of 65 ~ 70 °C before deposition. Scale bar represents 20 mm.

<table>
<thead>
<tr>
<th>Type of micro – crystals</th>
<th>Estimated chemical formula</th>
<th>Estimated molecular weight (g * mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH$_3$NH$_3$PbI$<em>2$Br$</em>{0.4}$</td>
<td>601.18</td>
</tr>
<tr>
<td>B</td>
<td>(CH$_3$NH$<em>3$)$</em>{0.86}$(CH(NH$_2$)$<em>2$)$</em>{0.14}$PbI$_3$</td>
<td>621.80</td>
</tr>
<tr>
<td>C</td>
<td>(CH$_3$NH$<em>3$)$</em>{0.86}$(CH(NH$_2$)$<em>2$)$</em>{0.14}$PbI$<em>2$Br$</em>{0.2}$</td>
<td>612.40</td>
</tr>
<tr>
<td>D</td>
<td>CH$_3$NH$_3$PbI$_3$</td>
<td>619.98</td>
</tr>
</tbody>
</table>

Table 2.4: Type of doped or undoped CH$_3$NH$_3$PbI$_3$ micro-crystals synthesised using the almost stoichiometric mechanochemical MC2 PbI$_2$ in reaction with equimolar plus an excess 10 % by weight of CH$_3$NH$_3$I and (A) 40 % moles of CH$_3$NH$_3$Br, (B) 14 % moles of CH(NH$_2$)$_2$I, (C) 14 % moles of CH(NH$_2$)$_2$I and 10 % moles of Br$_2$ and (D) no other dopant. Also, estimated chemical formula and molecular weight, is provided for each type.
2.4 Preparation of perovskite devices

2.4.1 Perovskite solar cells fabrication

Perovskite solar cell devices were fabricated by employing the n-i-p planar (regular) architecture, as graphically illustrated in figure 2.5. Glass substrates pre-patterned with six ITO (indium tin oxide) pixels (20 Ω / square, Ossila) were first cleaned by sonicating for 10 min in a solution made of 1 mL detergent (Hellmanex (III)) and 250 mL boiled deionised water (100 °C). Any residual detergent was subsequently washed off by rinsing the substrates three times with 100 mL (each time) of deionised water. The Glass / ITO substrates, were further sonicated two more times for 10 min (each time) in 250 mL acetone and then 250 mL isopropanol. The cleaned substrates were then treated with oxygen plasma using a Zepto surface plasma cleaner (model 8) at power of 100 watts and oxygen flow rate adjusted at 200 mbar for 10 min to remove organic contaminants. The clean glass / ITO substrates were then transferred into a cleanroom (class 1000) with constant temperature 20 °C and humidity 30 %, for deposition of the electron transporting layer and perovskite thin film. Commercially available colloidal dispersion of tin (IV) oxide (SnO₂) in deionised water (15 %, Alfa Aesar) was re-diluted in deionised water, in 1:4 volume ratio and then filtered with a PVDF filter with a pore size of 0.2 μm. Then 50 μL of re-diluted SnO₂ solution was spin coated at 3000 rpm for 30 s, followed by removal of the SnO₂ from part of the substrate using a dry cotton bud, re-exposing the ~ 4 - 5 mm ITO electrode. The coated substrates were then annealed at 150 °C for 30 min and cooled down to 20 °C, without any further treatment.⁶ 50 μL of the perovskite solutions made of either undoped or doped CH₃NH₃PbI₃ micro-crystals in DMSO with concentration 1.13 M or solutions of mechanochemical MC 2 or commercial PbI₂ reacted with equimolar amount of CH₃NH₃I in DMSO with concentration 2.8 M, were statically dispersed onto the glass / ITO / SnO₂ samples followed by spin coating. The spinning speed was 2500 rpm for all the solutions with concentration 1.13 M, while 3100 rpm spinning speed was used for the solutions with concentration 2.8 M. In all cases, the spinning time regardless of the speed was 10 s. Also, the concentration of solutions was adjusted in respect to the spinning speed towards the formation of CH₃NH₃PbI₃ thin films with reduced accumulation of material at the edges of substrate, as shown in figure 2.6. Immediately after the spin coating process, each substrate was placed in a custom-made vacuum
chamber for 120 s and pressure ~ 0.02 mbar, as shown in figures 2.7 a and 2.7 b. Then each substrate was annealed on a hot plate at 100 ºC for 30 s for crystallisation of perovskite. All glass / ITO / SnO2 / CH3NH3Pbl3 samples were then transferred inside a nitrogen filled glove box for the synthesis and deposition of doped hole transporting layer of 2,2',7,7'-Tetrakis [N,N-di (4-methoxyphenyl) amino]-9,9'-spirobifluorene (spiro-OMeTAD) (≥ 99.5%, Ossila). Then 86.6 mg of spiro-OMeTAD powder was dissolved in 1 mL of chlorobenzene. The solution was then doped with lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) (≥ 99%, Sigma Aldrich), 4-tert-butylpyridine (TBP) (96.6%, Sigma Aldrich) and FK209 (FK 209 Co(II) PF6), (Greatcell). The quantity of dopants used in 1 mL of the spiro-OMeTAD / chlorobenzene solution was as follows, 20 µL of Li-TFSI (500 mg*mL⁻¹ in acetonitrile), 34 µL of TBP and 11 µL of FK209 (300 mg*mL⁻¹ in acetonitrile). The solution was filtered with a PTFE filter with a pore size of 0.2 µm and then 50 µL was spin coated on each sample dynamically at 4000 rpm for 30 s. For perovskite solar cell devices, fabricated by doped CH3NH3Pbl3 micro-crystals synthesised using only the mechanochemical MC 2 PbI2 powder, the HTL layer (spiro-OMeTAD) was free of FK209 dopant agent. All the devices were left overnight in dry air to allow the Li⁺ cations to oxidise, since Li2O converts the spiro-OMeTAD into an enhanced p-type semiconductor. 7 Finally, gold electrodes with thickness ~ 80 nm, were deposited through a template mask using an Edwards thermal evaporator at pressure < 8 * 10⁻⁷ mbar, with a deposition rate 0.1 Å s⁻¹ for the first 2 nm and then 1 Å s⁻¹ for the remaining thickness.8 All un-encapsulated PSCs devices, as shown in figure 2.8, were immediately characterised electrically.

![Figure 2.5: Graphically illustration of ITO / SnO2 / Perovskite / Spiro – OMeTAD / Gold layers in perovskite solar devices with n-i-p planar (regular) architecture.](Image)

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Figure 2.6: Reduced accumulation of $\text{CH}_3\text{NH}_2\text{PbI}_3$ at substrate edges in respect to the spinning speed, scale bar represents 15mm.
Figure 2.7: The custom-made vacuum chamber consisting of a vacuum line connected to a rotary vane dual stage mechanical vacuum pump (Edwards), valve 1 regulating the pressure and valve 2 resetting the pressure to one bar in the vacuum chamber, respectively (a), scale bar represents 10 cm. Inside view of the vacuum chamber (b), scale bar represents 2 cm.

Figure 2.8: Image of complete un-encapsulated PSCs device with 6-pixel (individual) solar cells, scale bar represents 10 mm.
2.5 Characterization techniques

2.5.1 X-ray diffraction

X-ray diffraction (XRD) is a technique that is used to determine the atomic or molecular crystal structure of materials. The incoming electromagnetic beam of x-ray radiation is primarily scattered by the outer electrons of atoms in the sample producing secondary spherical waves by the elastic scattering effect. Since the atoms in the materials are arranged in planes within a crystal lattice, these spherical waves deconstructively interfere and cancel each other in the majority of directions, but in a few specific directions the spherical waves constructively interfere and are detectable, as shown in figures 2.9 a and 2.9 b. The arrangement of atoms in unit cells in materials define the degree of crystallinity, higher crystallinity results more repeated unit structures, whereas materials with low crystallinity (more amorphous) are characterized by low localized repeatability of the unit structure. In perfect crystals with high order crystallinity, atoms are placed in planes parallel to each other separated by a distance \( d_{hkl} \) (identified by the hkl Miller indices which determines their direction and distance in 3-dimensional space). The resulting constructive interference of spherical waves with the same phase takes place, if the path difference between the rays from consecutive planes, which is \( 2d_{hkl} \cdot \sin \theta \), is equal to an integer number of the x-ray wavelengths (\( \lambda \)) and obeys to the Bragg’s law, as shown in equation 2.7:

\[
n * \lambda = 2d_{hkl} * \sin \theta \quad \text{equation 2.7}
\]

![Figure 2.9: Schematic illustration of the XRD characterization in materials. When incident and diffracted x-ray beams are not in phase results (a) destructive interference, whereas if incident and diffracted x-ray beams are in phase results (b) constructive interference.](image)
The measured signal of diffracted x-ray intensity as a function of the scattered angle \((2\theta)\) provides information about the atom spacing between planes in the crystal structure and is affected by many factors. The relative intensity of the diffracted peaks is primarily ruled by the structural factor \(F_{hkl}\), in which \(f_n\) is the atomic scattering factor and \(u_n / v_n / w_n\) the unit cell's dimensions, as defined by the equation 2.8: \(^9,10\)

\[
F_{hkl} = \sum_{n=1}^{N} f_n \exp(2\pi i(hu_n + kv_n + lw_n)) \quad \text{equation 2.8}
\]

However, there are other factors influencing the x-ray diffracted intensity. In certain lattice structures, the spacing and arrangement of planes produces diffractions from groups of planes that are exactly 180\(^\circ\) out of phase, resulting in the phenomenon of extinction. Also, when a number of similar planes cut through a unit cell in a particular plane in a repeatable way, then it is called multiplicity. One more factor that affects the diffraction intensity as known the Lorentz factor, which occurs when a lattice point on the reciprocal lattice intersects the diffractometer that moves on the trajectory of a circle (x-ray detector). Additionally, phenomena of fluorescence and polarization, related with polyphase samples and monochromatic incident x-ray beam, introduces further factors of signal influence. Crystallite size also contributes to the nature of the diffraction peaks, for example in materials with small particle size the number of lattice planes may be insufficient for an effective destructive interference with respect to the scattering angles close to Bragg's angles, which results in deviation and broadening of the characteristic diffracted peaks. Finally, uniform and non-uniform strains (tensile or compressive forces) in the material can alter the crystal structure slightly and generate macrostrain effects, resulting in shifts, asymmetry and broadening of the diffracted peaks, as shown in figure 2.10. \(^11\) For our experiments a D2 Phazer (Bruker) diffractometer was used, with a monochromatic source of x-rays generated by a copper anode (Cu-k(\(\alpha\)) lines) with wavelength \(\lambda = 1.54184 \text{ Å}\), as schematically illustrated in figure 2.11. The samples were mounted in the holder, while the angle between the sample and the incident beam is \(\theta\), the detector maintained at an angle of 2\(\theta\), in respect to the incident beam of X-ray. Both divergence and receiving slits are kept at fixed positions during the measurement. The x-ray scattering intensity for PbI\(_2\) powders and undoped / doped CH\(_3\)NH\(_3\)PbI\(_3\) micro-crystals were measured as function of the 2\(\theta\) angle, with a step size 2\(\theta = 0.020273\ \text{o}\) over the 2\(\theta\) range from 9\(\text{o}\) to 52\(\text{o}\).
and an acquisition time of 0.4 s per step. Also, the x-ray scattering intensity for doped CH$_3$NH$_3$PbI$_3$ micro-crystals as function of the $2\theta$ angle, was measured with step size $2\theta = 0.020273$° degrees over the $2\theta$ ranges from 11° to 16°, 27° to 30° and 30° to 33° increasing the acquisition time to 0.9 s per step for higher resolution. All measurements of powders, were made using a zero - background holder made of monocrystalline silicon. All XRD data were plotted using Origin Pro v 8.1 software.

Figure 2.10: Schematic illustration of the applied strains in crystal structure and associated diffracted peak variability.
2.5.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is a characterization technique of samples made of various materials, that includes imaging and elemental analysis of specimens. In a typical SEM, a beam of electrons is accelerated by an applied voltage from a few 100V to ~25 kV and then passed through a series of electromagnetic lenses (condenser and objective lenses) before interacting with the sample. Incident electrons interact with the surface of the specimen, resulting in excitation of electrons from the sample. The sample and apparatus are kept under vacuum, in order to eliminate electron interactions with air or chemical molecules. Electrons scattered from the sample, after elastic and inelastic scattering events with the electrons of atoms in specimen are detected while the beam position scans the surface of the sample. The detected signal of electron intensity, is reconstructed by software, forming images with magnification within the range of ~10 to 10^6 times, as shown in figure 2.12. The resolution of collected SEM images is affected by many parameters. These include the thickness and electron transparency of the specimen and the accelerating voltage, which causes variability of the electron penetration into the specimen. This provides different mechanisms of interaction between the incident electrons and the atoms/electrons of the specimen, resulting in a range of emitted electrons and radiation categorized as Auger electrons (AE), Secondary electrons (SE), Backscattered electrons (BSE), x-rays (EDX) and Cathodoluminescence (CLE), which all have different escape depths.
from the specimen. This can be illustrated by the intercalation volume and expressed as the spatial distribution of electron trajectories inside the specimen, as shown in figure 2.13. The detection of those emitted electrons and radiation, is achieved by a range of detection sensors used in SEM. For example, SE provide topographical information of the samples’ surface and are emitted from the first ~100 nm in the sample with energies < 50 eV, based mainly on ionization phenomenon. Those SE can be effectively detected using a through lens detector (TLD) in a high-resolution immersion mode. During the immersion mode, emitted SE pass up through the electron column and can be selectively deflected by an array of electromagnetic coils before being detected by the SE detector mounted above the objective lens in a lateral position with respect to the electron column, as shown in figure 2.14. 

Some important features of using TLD imaging in SEM, is the low energy required for the accelerated electrons of the beam (< 2 keV) in combination with the minimum working distance (~ 2 - 4 mm) between the lower edge of electron column and specimen. Both these features provide sufficient detection of the low concentration of SE emitted from the specimen in a less destructive way, and resulting in maximum of contrast between features of different elemental composition or optoelectronic properties (such as the work function).

Figure 2.12: Schematic diagram of the main components of a scanning electron microscope (SEM). Electron source, anode, condenser/objective lenses consist the electron column.
Also, SEM is capable for elemental analysis known as energy dispersive x-ray spectroscopy (EDS), which is performed by measuring the energy and intensity distribution of the emitted x-rays generated by the specimen under a focused high accelerated beam of electrons with energy > 10 keV. The incident electrons from the beam, excite an electron from an inner shell creating an electron hole (vacancy). An electron from an outer shell with higher energy occupies that hole in the inner shell.
and the difference between the shell energies is emitted as an x-ray. These emitted x-ray energies are characteristic of the shell transitions of electrons in each type of atoms, allowing the correct detection of elements in specimens. However, EDS only provides a relative estimation of elemental composition, since multiple transitions of electrons between shells and emission of BSE and CLE introduce interfering effects for the detection of those characteristic x-rays. 13

For the experiments reported in this thesis, most of the SEM images and EDS (elemental analysis of points or in full images) from PbI₂ powders or perovskite microcrystals in chapter 3 and 4, were obtained using a JSM-6010LA (JEOL) at accelerating voltages 12 kV and 15 kV and working distance 10 mm, respectively.

Whereas, the single or sequential acquisition of TLD-SEM images were obtained using a FEI Helios NanoLab G3 UC SEM at accelerating voltage 2 kV using a TLD biased from 0 to 30 V with step size 0.2 V at working distance of 4.2 mm and with beam current of 13 pA. Also, a FEI Nova NanoSEM 450 was used at an accelerating voltage 1 kV using a TLD biased from 0 to 30 V with step size 0.2 V at working distance of 2 mm and with beam current of 15 pA. All SE images (single or sequential acquisition) in chapter 3, were obtained either by preparing pellets of PbI₂ with diameter ~ 13 mm under an applied press of 9 tons of mass or by preparing thin films of perovskite on cleaned glass. SE spectra were obtained after alignment of sequential TLD-SEM images and calculated using ImageJ v1.5e software, while all data were plotted using Origin Pro v 8.1 software.

2.5.3 Photocurrent density-voltage

Un-encapsulated perovskite solar cells with device structure glass / ITO / SnO₂ / CH₃NH₃PbI₃ / spiro-OMeTAD / Au were placed into the push fit test board with the glass side facing upward (Ossila Ltd). A shadow mask with six square apertures and an area of ~ 0.025 cm² per square was placed on top of the glass, the aperture pre-defining the area of the solar cells exposed to irradiation, as shown in figure 2.15. Solar cells were exposed to irradiation that corresponds to AM 1.5 G of the solar spectrum, simulated using a Newport 92251A-1000 solar simulator. Before electrical characterization of solar cell devices, the photon density was calibrated using a NREL
certified silicon reference cell at 100 mW * cm\(^2\) at 25 °C. Each cell was biased from -0.2 V to +1.2 V and then back to -0.2 V at a scan step of 0.1 V * s\(^{-1}\) measuring the current density employing a Keithley 237 as a source measure unit. The recorded data were plotted using Origin Pro v 8.1 software.

![Image of push fit test board from Ossila Ltd (on the top), perovskite solar cell device (at the bottom).](image)

**2.5.4 X-ray photoelectron spectroscopy**

X-ray photoelectron spectroscopy (XPS) is considered one of the most accurate characterization techniques for elemental or chemical composition in materials. The operating principle of XPS is based on the light-matter interaction, known as the photoelectric effect which was discovered by H. Hertz in 1887. By irradiating the specimen with monochromatic low energy photons ~ 1 – 2 keV (x-rays), photoelectrons are emitted originating from either by the atomic core shells or from the valence band. The kinetic energy of the emitted photoelectrons is determined by equation 2.9, in which KE is the measured kinetic energy of the excited electrons, hv the incident energy of x-rays, BE the binding energy of the core shell electron in respect to the Fermi level and \(\Phi_S\) is the spectrometer work function, as shown in figure 2.16.

\[
KE = hv - BE - \Phi_S \tag{2.9}
\]
Figure 2.16: Illustration of photoemitted electron from 2p atomic orbital by x-ray photon.  

$\Phi_S$ is the energy required to promote the electron from the highest occupied electronic level to the unbound state with zero kinetic energy (vacuum level). Also, during XPS characterization of specimens, the photo-ionized atom returns to a more stable energy state, either by filling the hole of the photoelectron emitted with an electron from a higher core shell level accompanied by emission of characteristic to the transition x-ray, or by emitting an Auger electron. An Auger electron is ejected, when the core hole is filled with an electron from a higher core shell without the emission of characteristic to the transition x-ray. In a typical XPS spectra, binding energy versus electron intensity is plotted, independent of the incident x-ray energy used during the measurement. The resulting peak positions correspond to specific elements as a function of the binding energy and their intensity reflects the atomic concentration. The intensity of each peak is given approximately by the Beer – Lambert law (as shown in equation 2.10) and expresses the probability of the photoemitted electron to reach the surface of specimen and be detected.

\[ I_d = I_0 \ e^{\left(\frac{-d}{\lambda \cdot \cos \theta}\right)} \]  

equation 2.10
Where \( I_d \) is the photoemitted electron density in respect to escape depth \( d \) from specimen, \( I_0 \) is the incident intensity of electrons, \( \lambda \) is the electron inelastic mean free path (IMFP) and \( \theta \) is the angle of the photoemitted electron with respect to the specimen surface. The IMFP statistically is the average distance that a photoemitted electron can travel inside the material before any inelastic scattering event occurs and depends on the specimen density and the KE of the electron. In XPS, high energy resolution of the characteristic peak of elements is required. The resulting spectra collected contain a series of peaks that are defined by the full width at half maximum (FWHM), which is a convolution of the x-ray characteristic line width, the width of the photoemitted electron lines, surface charging and the analyser / detector resolution. Typically, in XPS the x-ray sources used are based on either monochromator (aluminium) or dual (aluminium and magnesium) anode-targets. Anode-targets are made of aluminium, which have a \( k(\alpha)_{1,2} \) transition with energy of 1486.6 eV and FWHM of 0.85 eV, while magnesium targets have a \( k(\alpha)_{1,2} \) transition with energy of 1253.6 eV and FWHM of 0.7 eV. The different FWHM in terms of energies of both anodes provide different energy resolution in the resulting XPS spectra, since the x-ray monochromator allows reduction of the unwanted x-ray satellites and Auger electrons. Photoemitted electrons are passing through the concentric hemispherical energy analyser before being retarded by biased apertures and their kinetic energy being measured by the detector, as graphically illustrated in figure 2.17.

![Diagram of XPS spectrometer](image)

*Figure 2.17: A graphical illustration of an XPS spectrometer equipped with monochromator or dual anode x-ray source, retardation aperture, concentric hemispherical energy analyzer and detector.*
XPS instruments require regular calibration to secure accurate measurement of the binding energy of elements. Calibration is achieved by measuring specific samples which are made of gold. The recorded XPS spectra are divided into two groups: the main low energy resolution survey spectra and the high energy resolution spectra for the accurate quantitative analysis of the elements of interest. Additionally, quantitative analysis of elements in XPS spectra requires the introduction of the Schofield relative sensitivity factors (RSF) and characteristic transmission functions for the analyser as provided by the National Physical Laboratory (NPL) for normalization of the photoemitted electron intensities of all the elements present in specimen.\textsuperscript{15,16} For the experiments reported here, mechanochemical or solvothermal or commercial PbI\textsubscript{2} powder was mounted for analysis by pushing the powder into indium foil. The indium foil was then placed directly onto the sample holder using double sided conducting carbon tape. The analysis was carried out using a Kratos Supra instrument with a monochromatic aluminium source of x-rays with energy of 1486.69 eV. Low energy resolution survey scans were collected between binding energies from 1200 to 0 eV, at 1 eV intervals with an acquisition time of 10 min (per point) from two analysis points per sample. While high energy resolution scans were also collected for the I 3d, O 1s, C 1s and Pb 4f core levels, at 0.1 eV intervals with an acquisition time of 5 min, for each point. The data collected were calibrated in intensity using a transmission function characteristic of the instrument to make the values instrument independent. All data were then quantified using the CasaXPS software. Binding energy calibration of all the low energy resolution survey scans or high energy resolution scans was conducted with respect to the Pb 4f\textsubscript{7/2} core level at 138.0 eV. No escape depth correction was applied at each low energy resolution survey or high energy resolution scans, before starting any further quantification analysis.\textsuperscript{17} For the compositional analysis of the core level spectra of I 3d\textsubscript{5/2}, O 1s, C 1s and Pb 4f\textsubscript{7/2}, the Scofield relative sensitivity factors of 16, 2.52, 1 and 13.7 were used, respectively. The binding energy regions used for analysis, were kept constant with respect to each element at each low energy resolution survey or high energy resolution scans. Also, for each binding energy region, a Shirley type background function was used. The resulting data were plotted using Origin Pro v 8.1 software.
2.5.5 Rutherford backscattering spectroscopy

Rutherford backscattering spectroscopy (RBS) is considered one of the most accurate characterization techniques for elemental analysis in depth or near the surface of materials. Initially, in 1911 Ernest Rutherford first experimentally determined the existence of atomic nuclei by measuring the backscattered alpha particles from gold foil. Since then, tremendous development has been made in apparatus and data analysis related to RBS. In principle, the specimen (target) is installed and bombarded at specific angles (5° – 15°) with respect to the beam of highly accelerated particles of helium ions (\(^{4}\text{He}^+\)) within the energy range from 0.5 to 3 MeV. The energy loss of the backscattered particles caused by the interaction with the nuclei within the target, which depends on the atomic number Z of each element in the target, is recorded by a solid-state detector at scattering angles (θ) from 150° to 170°, resulting in the quantitative determination of elemental composition in materials, as graphically illustrated in figure 2.18. Some of the advantages of RBS technique are the absence of the need for a reference sample, in depth resolution of elemental composition of the order of 0.2 – 20 μm and the high detection resolution of heavy elements. Whereas, a significant disadvantage of RBS is the low detection resolution of light elements (in comparison with the heavier elements). Since the only mechanism of energy loss during the RBS measurement is the momentum transfer from incident particles to the target’s nuclei, the energy ratio of incident particles before and after interaction with specimen is known as the kinematic factor (K) and given by the equation 2.11. In which, \(M_1\) is the mass of incident particles, \(M_2\) the mass of nuclei in the specimen and \(θ\) the scattering angle.
Figure 2.18: Graphically illustration of Rutherford backscattering spectroscopy characterization technique.\textsuperscript{18}

\[ K(\theta, M_1, M_2) = \frac{E_1}{E_0} = \left( \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_1 + M_2} \right)^2 \text{ equation 2.11} \]

As the mass of atoms in the target increases, the energy of the backscattered particles progressively approaches the energy of the incident particles. Also, during analysis of specimens with RBS as a characterization technique, some important parameters must be considered. The first important parameter is related to the energy limit of the incident particles that interact with the specimen. If highly accelerated incident particles interact with the nuclei of atoms surpassing the Coulomb barrier, the resulting nuclear reactions with the target can create radioactive isotopes. An empirical formula that provides the maximum energy of the incident particles as given by the equation 2.12, is regarded for elimination of those undesirable nuclear reactions. Where \( E_0 \) is the kinetic energy of the incident particles in MeV, \( Z_1 / M_1 \) and \( Z_2 / M_2 \) are the atomic numbers and nuclei masses of incident particles and of the atoms in specimen (average values of the \( Z_2 / M_2 \) are considered for multi-elemental specimens), respectively.
\[ E_0 < \frac{Z_1 Z_2}{M_1^{1/3} + M_2^{1/3}} \]  

equation 2.12

The second parameter that must be considered, the cross section, is related to reduced probability of scattering events in the detector direction. Generally, scattered particles with trajectories out of detector position, are following directions at an angle of either forward (\( \Phi < -90^\circ \)) or backward (\( \Phi < +90^\circ \)), as shown in figure 2.19. By definition the cross section of scattered incident particles has got multiple impacts during the RBS characterization of specimens. Mainly affecting the number of backscattered particles from the target’s nuclei, the position of the solid-state detector for maximum backscattered particles detection and the kinetic energy of the incident particles. For our experiments a 1.7 MV Tandetron RBS linear type tandem ion-beam accelerator was used, which is located in the Laboratory of Ion Beam Physics at the ETH Zurich facilities in Switzerland. Commercial and synthesized PbI\(_2\) pellets, with diameter ~ 13 mm and thickness ~ 1.5 mm, were prepared under an applied press of 9 tons of mass and measured using accelerated ions of \(^4\)He\(^+\) at 2 MeV, while a PIN diode detector was placed at angle 168° with respect to the ions of incident beam. The resulting data were plotted using the RUMP simulation software.

Figure 2.19: Schematic diagram of trajectories with corresponding angles for forward (\( \Phi < -90^\circ \)) and backward (\( \Phi < +90^\circ \)) scattered particles. 18
2.5.6 Atomic force microscopy

Atomic force microscopy (AFM) is a non-destructive characterization technique for high resolution topographical imaging of various materials (solid – organic – liquid - biological samples etc.). In principle, AFM surface imaging is based on the weak interactions between a tip and the surface of specimen, as invented by Gerd Binning et al. in 1986. Typically, an AFM consisted of a laser diode for spot positioning, a cone-shaped small tip (probe) made of silicon or silicon nitride positioned on the free end of a cantilever, a piezoelectric module for positioning and height movements of the cantilever allowing scanning of the tip over the specimen in three directions (X – Y – Z) and a four-quadrant positioning photodiode, as shown in figure 2.20.

![Figure 2.20: Schematic diagram of atomic force microscope (AFM) components.](image_url)

When the probe approaches and scans the surface of specimen in X – Y directions, repulsive and attractive interactions based on Coulomb and Van der Waals forces respectively, causes vertical bending of the cantilever with respect to the surface of specimen, as shown in figure 2.21. Different modes of materials characterization in AFM (contact / tapping / no contact) utilise different regions within this plot of probe sample interactions.
These vertical diversions of the cantilever result a weak displacement in the laser beam spot being detectable by the four-quadrant positioning photodiode. The signal (voltage) fluctuation generated by the photodiode during the scanning process of the specimen is processed and reconstructed as a topographical image by specific software. The geometry and materials used for the construction of the cantilever and probe, combined with the scanning velocity, affect the resolution of acquired topographical images. The characteristic spring constant that relates to the material and geometry of cantilever. The cantilever obeys to the Hooke’s law, as given in equation 2.13. Where $F$ is the resulting force, $k$ the cantilever constant and $y$ the vertical diversion of cantilever.  \(^{20}\)

$$F = -k \times y$$ \hspace{1cm} \text{equation 2.13}

For our experiments, roughness and thickness measurements of perovskite thin films were performed using a Dimension icon with ScanAsyst AFM (Bruker) with a cantilever consisting of a silicon probe on a silicon nitride cantilever (Bruker) with characteristic properties ($f = 70$ kHz, $k = 0.4$ N * m\(^{-1}\)). AFM data analysis was conducted by using Nanoscope Analysis v 1.3 software.
2.5.7 Visible-infrared (Vis-IR) spectroscopy

Visible-infrared (Vis-IR) spectroscopy is a non-destructive characterization technique, based on light - matter interactions. Generally, there are different mechanisms of light absorption in semiconductors, such as inter-band, dopant, excitonic, by charge carriers and crystal lattice. However, the intra-band light absorption is considered as the fundamental mechanism, resulting in the determination of the optical band gap in semiconductors. The minimum energy of a photon (quantum) that is sufficient to excite an electron from the highest level of the valence energy state (valence band) to the lowest level of the conduction energy state (conduction band), is equal to the band gap (E_g) in semiconductors. Also, semiconductors with indirect E_g require increased number of absorbed photons, due to the need for the presence of a crystal lattice oscillation (phonon) during the absorption of a photon, in comparison with a semiconductor with direct E_g. The minimum absorbed energy required by the semiconductor is related to the wavelength by the Planck equation, as shown in equation 2.14. In which, h is Planck’s constant, c the speed of light in vacuum and λ is the wavelength of photons that correspond to the absorption edge of semiconductor.

\[ E_g = \frac{h*c}{\lambda} \]  

Also, the distribution of allowed electron transitions in semiconductors with either direct or indirect band gap, are described by the absorption coefficient (a), as shown in equations 2.15 and 2.16, respectively. In which, E_photons is the energy of incident photons and A and B are constants not related to the light absorption.

\[ a_{direct} = \frac{A}{E_{photons}} \left( E_{photons} - E_g \right)^{1/2} \]  

\[ a_{indirect} = \frac{B}{E_{photons}} \left( E_{photons} - E_g \right)^2 \]  

The dependence between absorption coefficient and wavelengths can be used to accurately determination of the E_g from a graphical fitting process using a Tauc plot. In addition, the absorption coefficient (a) in semiconductors with either direct or indirect
band gap is determined by the Urbach energy ($E_U$), which is related to the degree of structural disorder (defects), as given in equation 2.17. In which $a_0$ is a constant.

$$a_{(\text{direct or indirect})} = a_0 \times \exp\left(\frac{h \times c - E_g}{E_U}\right)$$  \text{equation 2.17}

For our experiments, absorption spectra of perovskite thin films deposited on clean glass, were obtained using a spectrometer (USB2000 + UV – VIS – ES) equipped with a deuterium halogen light source (UV – VIS - NIR_DT – MINI – 2 - GS), both from Ocean optics. Data were collected using the Ocean Optics SpectraSuite software and the recorded data were plotted using Origin Pro v 8.1 software. 21

2.6 References


Chapter 3

Implications of stoichiometry and polytypism in $\text{PbI}_2$ used to fabricate perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$)

3.1 Introduction

The improvement in photovoltaic performance of perovskite solar cells (PSCs) as the next potential candidate of a low-cost conversion technology of solar power to electricity has been tremendous. Devices based on one of the most studied hybrid organic / inorganic perovskites, known as methylammonium lead triiodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), have seen their power conversion efficiencies (PCE) rocket from 3.8 % to 21.2 % in a decade.$^{1,2}$ Mixtures of organic and inorganic cations, predominantly methylammonium, formamidinium and caesium ($\text{MA}^+ / \text{FA}^+ / \text{Cs}^+$) with various halogen anions, such as chloride, bromide and iodide ($\text{Cl}^- / \text{Br}^- / \text{I}^-$) have been incorporated to improve the stability in PSCs. However, long term stability and durability in PSCs have remained barriers to their commercialisation. These effects might be related to deficiency of the iodide in the crystal structure of perovskite as presented by Jacobsson et al., Graetzel et al. and an optimum tolerance factor closer to unity that corresponds to the cubic crystal structure as presented by Saliba et al.$^{3-7}$ This degradation occurs regardless of the device architecture configuration utilised (p-i-n or n-i-p).$^8$ In this chapter is described in detail the importance of stoichiometry and polytypism present in $\text{PbI}_2$ used for fabrication of PSCs based on $\text{CH}_3\text{NH}_3\text{PbI}_3$, two properties that might be related to the mechanism of degradation and poor stability in PSCs. Determination of the polytypes present and the stoichiometry of $\text{PbI}_2$ powders synthesised by solvothermal and mechanochemical routes have been compared to commercially available $\text{PbI}_2$ powders. This was accomplished using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering
spectroscopy (RBS) and controlled synthesis of CH$_3$NH$_3$PbI$_3$ micro-crystals. Also, we show that the use of commercial sub-stoichiometric PbI$_2$ for the formation of CH$_3$NH$_3$PbI$_3$ might results in unreacted PbI$_2$ as determined by Vis-IR spectroscopy and the presence of the impurity is reflected in terms of PCE in the fabricated PSCs. The presence of unreacted PbI$_2$ (~ 10 %) causes an average PCE reduction of the PSCs from ~ 15.5 % to ~ 4.6 %.

3.2 Results and discussion
3.2.1 EDS analysis of PbI$_2$ powders

PbI$_2$ powders synthesized by solvothermal (ST) and mechanochemical (MC) routes were characterized by scanning electron microscopy (SEM) and integrated energy dispersive spectroscopy (EDS). ST synthesis of PbI$_2$ resulted in the formation of needle shaped crystals on top of hexagonal PbI$_2$ platelets, as shown in figure 3.1 a. The incorporation of oxygen was detected in these needles as indicated by EDS analysis from 3 points, is possibly attributed to autoionization of water molecules caused by strong Coulomb interactions between the ions (Pb$^{2+}$ and I$^-$) and water molecules. This results in the formation of a mixture of lead oxyiodide and lead iodide hydroxide compounds, with the general chemical formulae Pb(I$_1$-$x$O$_x$)$_2$ and Pb(I$_1$-$y$(OH)$_y$)$_2$, respectively.$^{9-11}$ Whilst an absence of oxygen was detected from a single point on top of the PbI$_2$ platelet, as shown in table 3.1. In order to avoid the incorporation of oxygen from water, MC synthesis of PbI$_2$ was selected. This free of water process may reduce the concentration of the needle shaped crystals formed. MC synthesis of PbI$_2$ powder exhibited characteristic fragmentation and deformation of the PbI$_2$ platelets with an average size smaller than 4 μm, as shown in figure 3.1 b. While, no oxygen was detected in the MC PbI$_2$ platelets, as indicated by EDS analysis and shown in table 3.1. Also, for the commercially available powders from Sigma Aldrich (SA) and Tokyo Chemical Industries (TCI), the PbI$_2$ platelets had an average size smaller than 25 μm and 20μm, as shown in figures 3.1 c and 3.1 d, respectively.
Figure 3.1: Scanning electron microscopy (SEM) images of lead iodide powders as synthesised by (a) solvothermal (ST) and (b) mechanochemical (MC) routes, or commercially available from (c) Sigma Aldrich (SA) and (d) Tokyo Chemical Industries (TCI), scale bars represent 10μm.
<table>
<thead>
<tr>
<th>Points</th>
<th>Solvothermal (ST)</th>
<th>Mechanochemical (MC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Carbon</td>
<td>12.37%</td>
<td>15.68%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8.93%</td>
<td>7.42%</td>
</tr>
<tr>
<td>Iodide</td>
<td>38.68%</td>
<td>41.32%</td>
</tr>
<tr>
<td>Lead</td>
<td>40.02%</td>
<td>35.58%</td>
</tr>
</tbody>
</table>

Table 3.1: Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) atomic percentage composition of lead iodide, synthesised by solvothermal (ST) or mechanochemical (MC) methods.

3.2.2 X-ray diffraction analysis of PbI$_2$ powders

Different PbI$_2$ powders, one synthesised by the ST method and several by the MC method at various speeds of rotation and duration times during the planetary ball milling process (MC1: 200 rpm / 2 hours, MC2: 400 rpm / 1 hour and MC3: 400 rpm / 4 hours) were characterised by XRD and compared with two commercially available PbI$_2$ powders of high purity, one from Sigma Aldrich with purity 99.999% (SA) and the second one from Tokyo Chemical Industries with purity 99.99% (TCI). Significant differences in the XRD patterns were observed between the commercial SA, TCI, ST and mechanochemical MC1 / MC2 / MC3 PbI$_2$ powders, as shown in figure 3.2. Also, for better clarity, the detected XRD peaks were categorized into two groups of peaks based on the diffracted 2θ angle and the Miller indices of the corresponding crystallographic planes. Peaks with Miller indices of planes (001), (002) and (003), form the primary group (indicated by the red colour in figure 3.2), while the (100), (101), (102), (110), (111), (103) and (201), form the secondary group (indicated by the green colour in figure 3.2) and summarized in table 3.2. Based on the International Centre for Diffraction Database, the primary XRD peaks correspond to the 2H polytypic phase of the PbI$_2$ with code (01-071-6147), while the secondary XRD peaks, correspond mainly to a mixture of 4H (04-017-4470), 14H (04-007-2277) and 20H (04-007-2278) polytypic phases, with characteristic c axis unit cell dimensions 1.3962 nm, 4.8853 nm and 6.979 nm, respectively. However, the possibility of undetected minor fractions of PbI$_2$ crystallised in a rhombohedral structure cannot be excluded.
Figure 3.2: XRD patterns of commercial Sigma Aldrich (SA), Tokyo Chemical Industry (TCI), solvothermal (ST) and mechanochemical at different conditions (MC1 to 3) PbI₂ powders. Normalization of XRD patterns, was in respect to (001) peak in all spectra. Peaks with the red in colour Miller indices indicating the crystallographic planes (001), (002) and (003) correspond to 2H polytypic phase, whereas Peaks with the green in colour Miller indices indicating the crystallographic planes (100), (101), (102), (110), (111), (103) and (201) correspond to mixture of 2H – 4H – 14H and 20H polytypic phases.

<table>
<thead>
<tr>
<th>Peak group</th>
<th>Miller indices</th>
<th>2-theta (degrees)</th>
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</thead>
<tbody>
<tr>
<td>Primary</td>
<td>(001)</td>
<td>12.74</td>
</tr>
<tr>
<td>Secondary</td>
<td>(100)</td>
<td>22.60</td>
</tr>
<tr>
<td>Primary</td>
<td>(002)</td>
<td>25.56</td>
</tr>
<tr>
<td>Secondary</td>
<td>(101)</td>
<td>25.98</td>
</tr>
<tr>
<td>Secondary</td>
<td>(102)</td>
<td>34.32</td>
</tr>
<tr>
<td>Primary</td>
<td>(003)</td>
<td>38.70</td>
</tr>
<tr>
<td>Secondary</td>
<td>(110)</td>
<td>39.58</td>
</tr>
<tr>
<td>Secondary</td>
<td>(111)</td>
<td>41.70</td>
</tr>
<tr>
<td>Secondary</td>
<td>(103)</td>
<td>45.27</td>
</tr>
<tr>
<td>Secondary</td>
<td>(201)</td>
<td>47.92</td>
</tr>
</tbody>
</table>

Table 3.2: Peak group, Miller indices and XRD diffracted angle (2-theta) of the lead iodide.
Based on the collected XRD spectra, the mechanochemical MC1 PbI₂ powder, did not display strong diffraction at the corresponding secondary XRD peak positions, indicating that MC1 has mainly crystallised in a single polytypic phase similar to that of SA sample. Whereas, mechanochemical MC2 and MC3 PbI₂ powders, display enhanced diffraction intensity at the corresponding secondary XRD peak positions, mostly caused by the higher speed of rotation and not the time duration during the planetary ball milling process. Also, the presence of those three additional polytypic phases in the mechanochemical MC2 and MC3 PbI₂ powders, makes them more comparable with the polytypic phases present in the TCI PbI₂ sample. It is presumed that, the formation of different polytypic phases during the growth of the PbI₂ platelets using the planetary ball milling process, is correlated to the amount of kinetic energy transferred to the reactant powders trapped between the colliding stainless - steel spheres during inelastic collisions.

3.2.3 XPS analysis and stoichiometry in PbI₂

XPS characterization was conducted for determination of the oxygen content and lead to iodide ratio of the commercial SA, TCI, ST and mechanochemical MC1 / MC2 / MC3 PbI₂ powders. The calculated ratios between the lead and iodide based on the average values from two different points of analysis on specimens indicated significant variation in the stoichiometry of the PbI₂ powders and the amount of oxygen, as summarised in table 3.3. In the SA material, the lead to iodide ratio was less than the stoichiometric 1 : 2. Whereas, for the TCI, ST, MC1 and MC3 PbI₂ samples the lead to iodide ratio was above the stoichiometric 1 : 2. Only the MC2 PbI₂ sample was shown to have an almost stoichiometric ratio between the lead and iodide atoms. This variation has been attributed to the different parameters of synthesis used, primarily the speed of rotation and secondarily the time duration, during the complicated planetary ball milling process.¹² Also, the higher percentage of oxygen amount detected in the ST sample, in comparison with all the MC synthesised PbI₂ powders, possibly attributed to the formation of the lead oxyiodide and lead iodide hydroxide compounds, as a result of the presence of water in the solvothermal method. The oxygen content was also tentatively manipulated in the mechanochemical MC3 sample. In contrast to the MC1 and MC2 PbI₂ samples, which were synthesised with the presence of air. For the MC3, the air was displaced inside the ball milling jar with argon gas of purity 99 %, which
resulted in an oxygen reduction by \( \sim 36 \, (\pm 10) \% \), in comparison with the rest of the mechanochemical samples synthesised without the introduction of argon gas. It is assumed further oxygen reduction in the mechanochemically synthesised \( \text{PbI}_2 \) powders, might be achievable by drying the reactants in a vacuum oven at temperature of 50 °C for 24 hours and simultaneously by displacing the air with ultra-pure argon gas (> 99.99 %) inside the ball milling jar.

<table>
<thead>
<tr>
<th>Lead iodide sample</th>
<th>Synthesis conditions/sample information</th>
<th>Ratio of Pb:I</th>
<th>Amount of oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC1</td>
<td>Mechanochemical (200 rpm 2 hours)</td>
<td>1:2.1 (± 0.1)</td>
<td>5.2 (± 0.8)</td>
</tr>
<tr>
<td>MC2</td>
<td>Mechanochemical (400 rpm 1 hour)</td>
<td>1:2.00 (± 0.1)</td>
<td>4 (± 0.2)</td>
</tr>
<tr>
<td>MC3</td>
<td>Mechanochemical (400 rpm 4 hours)</td>
<td>1:2.1 (± 0.1)</td>
<td>2.9 (± 0.1)</td>
</tr>
<tr>
<td>ST</td>
<td>Solvothermal (in water)</td>
<td>1:2.1 (± 0.1)</td>
<td>7.2 (± 0.2)</td>
</tr>
<tr>
<td>TCI</td>
<td>Tokyo Chemical Industries 99.99%</td>
<td>1:2.3 (± 0.1)</td>
<td>4.5 (± 0.1)</td>
</tr>
<tr>
<td>SA</td>
<td>Sigma Aldrich 99.999%</td>
<td>1:1.7 (± 0.1)</td>
<td>4.9 (± 0.1)</td>
</tr>
</tbody>
</table>

Table 3.3: The stoichiometric ratios between lead and iodide and amount of oxygen in commercial (SA and TCI), solvothermal (ST) and mechanochemically synthesized under three different conditions (MC1, MC2 and MC3) \( \text{PbI}_2 \) powders. All values correspond to the average numbers from two different points of analysis determined by high resolution XPS scans (a survey scan followed by high resolution scans was used for all samples).

Also, it should be clarified that the lead to iodide ratio and amount of oxygen were determined based on the average values that correspond to the intensity of photoexcited electrons from the Pb 4f 7/2, I 3d 5/2 and O 1s core levels, were accompanied by localised deviation from point to point, due to the inhomogeneous crystal structure of the more than one polytypic phases present in \( \text{PbI}_2 \) powders. This crystal structure inhomogeneity affects the relative intensity of the emission peaks as a consequence of the signal attenuation from the scattered electrons that varies as function of the kinetic energy of the emitted electrons. Additionally, it was found from
the XPS spectra acquisition sequence used (survey scan followed by high resolution scans or single high-resolution scan) can introduce variations between the lead to iodide ratio. A possible mechanism of that variation might be correlated to sublimation of iodide atoms from the PbI₂ powder as function of the interactions with the energy given by x-rays, resulting in an enhanced signal that corresponds to metallic lead. This effect was evaluated by comparing a survey scan followed by a high-resolution scan and a single high-resolution scan without any survey scan collected from two identical TCI PbI₂ powders, as shown in figures 3.3 a and 3.3 b, respectively. The lead to iodide ratio in the TCI PbI₂ sample was 1 : 2.3 (± 0.1), when a survey scan followed by high-resolution scan were conducted as signal acquisition modes. Whereas, the lead to iodide ratio was 1 : 2.4 (± 0.1) when a single high-resolution scan was conducted as a signal acquisition mode. Therefore, exact determination of the lead to iodide ratio in PbI₂ powders using XPS characterisation was laboured and the extracted data are considered only for a general trend between the lead to iodide ratios.

![Figure 3.3: XPS high-resolution spectra of Pb 4f 7/2 core level and metallic lead for the TCI lead iodide from different scanning modes. (a) survey scan followed by high-resolution scan and (b) single high-resolution scan.](image)

However, further research is required to better understand the impact of using over-stoichiometric PbI₂ material (such as TCI, MC1 or MC3) for the fabrication of PSCs.
devices. Over-stoichiometric PbI2 material enriched with iodide, might result in a gradient of accumulated iodide into the perovskite grains or at the grain boundaries. That localised agglomeration of iodide may affect the optoelectronic properties of perovskite, causing a reduction in the PSC performance which can vary with respect to the operating conditions, such as the presence of oxygen, inert gas or moisture. Also, excess iodide originated by the incorporation of an additional either >10% moles of PbI2 or >5% moles of CH3NH3I into the PSC devices with CH3NH3PbI3 as photoactive material, reduces the PCE as indicated by Carmona et al. and Zhang et al. Furthermore, diffusion of excess iodide might interact with the additional layers, such as hole and electron transporting layers or metallic contacts and contribute to their accelerated degradation through secondary chemical reactions.

3.2.4 Determining the stoichiometry in PbI2 by RBS

Rutherford backscattering spectroscopy (RBS) characterization was also conducted for determination of the lead to iodide ratio of the commercial SA, TCI, ST and mechanochemical MC1 / MC2 / MC3 PbI2 powders. The calculated ratios between the lead and iodide atoms based on a single point of analysis on each specimen, are summarised in table 3.4. All values contain 4 % systematic error, due to the uncertainty in stopping power of accelerated ions of 4He+ with energy 2 MeV during the RBS characterization. Also, RBS spectra of all PbI2 samples, are shown in figure 3.4. The lead to iodide ratio in the SA PbI2 sample was 1 : 1.9 (± 0.008), whereas the same ratio in all other samples was either identical (such as in the ST) or contain an excess of iodide. Also, calculated ratios between the lead and iodide atoms in all PbI2 samples based XPS and RBS characterization were quantitatively summarized in column graph, as shown in figure 3.5. Is noticeable that the number of iodide atoms in SA PbI2 is below the optimum 1:2 ratio in both characterization techniques. Whereas, the number of iodide per lead atoms is closer to the optimum ratio (1:2) in MC2 PbI2 and both the characterization techniques indicated very similar numerical values of iodide atoms in comparison with every other PbI2 sample (SA / TCI / ST / MC1 / MC3). That possible related with the different interaction of photons (in XPS) and ions (in RBS) with the lead and iodide atoms and their penetration depth in PbI2 samples which might related with a formatted gradient of iodide atoms between the surface and bulk (inner volume) directly correlated with the polytypic nature of PbI2.
<table>
<thead>
<tr>
<th>Lead iodide sample</th>
<th>Synthesis conditions/ sample information</th>
<th>Ratio of Pb:I</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC1</td>
<td>Mechanochemical (200 rpm 2 hours)</td>
<td>1:2.029 (± 0.007)</td>
</tr>
<tr>
<td>MC2</td>
<td>Mechanochemical (400 rpm 1 hour)</td>
<td>1:2.002 (± 0.008)</td>
</tr>
<tr>
<td>MC3</td>
<td>Mechanochemical (400 rpm 4 hours)</td>
<td>1:2.050 (± 0.007)</td>
</tr>
<tr>
<td>ST</td>
<td>Solvothermal (in water)</td>
<td>1:2.000 (± 0.007)</td>
</tr>
<tr>
<td>TCI</td>
<td>Tokyo Chemical Industries 99.99%</td>
<td>1:2.009 (± 0.007)</td>
</tr>
<tr>
<td>SA</td>
<td>Sigma Aldrich 99.999%</td>
<td>1:1.900 (± 0.008)</td>
</tr>
</tbody>
</table>

Table 3.4: The stoichiometric ratios between lead and iodide in commercial (SA and TCI), solvothermal (ST) and mechanochemically synthesized under three different conditions (MC1, MC2 and MC3) PbI₂ powders. All values correspond to a single point of analysis determined by Rutherford backscattering spectroscopy.
Figure 3.4: Rutherford backscattering spectra (RBS) from PbI₂ pellets made of commercial SA (a), TCI (b), solvothermal ST (c), mechanochemically MC1 (d), MC2 (e) and MC3 (f) synthesized under three different conditions.
3.2.5 Determining the stoichiometry in PbI$_2$ by XRD

A series of samples of CH$_3$NH$_3$PbI$_3$ micro-crystals were synthesised and characterised by XRD to further evaluate the stoichiometric ratio between lead and iodide in the sub-stoichiometric SA and the almost stoichiometric MC2 samples as determined by XPS analysis and previously discussed. The method of 1-pentanol / PbI$_2$ / CH$_3$NH$_3$I was used to synthesise CH$_3$NH$_3$PbI$_3$ micro-crystals with different controlled excesses by weight of CH$_3$NH$_3$I. This approach to stoichiometry determination in the PbI$_2$, is based on the critical amount of iodide ions introduced through the excess of CH$_3$NH$_3$I needed to result in complete elimination of the unreacted PbI$_2$ during the synthesis of CH$_3$NH$_3$PbI$_3$ micro-crystals. The XRD spectra of the corresponding synthesised CH$_3$NH$_3$PbI$_3$ micro-crystals after the reaction of the sub-stoichiometric SA with an excess by weight of CH$_3$NH$_3$I (10 %, 15 %, 20 % and 25 %) for 24 hours at constant temperature of 90 ºC, are shown in figures 3.6 a and 3.6 b. When 20 % excess by
weight of CH$_3$NH$_3$I was used in reaction with the sub-stoichiometric SA PbI$_2$ powder, results in a weak XRD peak at diffracted angle 2$\theta$ = 12.74$^\circ$ (indicated with an asterisk) that corresponds to a small fraction of unreacted PbI$_2$, as shown in figure 3.6 b. Consequently, the preferred excess by weight of CH$_3$NH$_3$I amount used in reaction with the sub-stoichiometric SA for absolute elimination of the unreacted PbI$_2$ during the synthesis of the CH$_3$NH$_3$PbI$_3$ micro-crystals, should be slightly greater than 20%. Also, the excess added iodide ions introduced in the reaction by the 20% excess amount by weight of CH$_3$NH$_3$, is comparable with the 10% excess of PbI$_2$ found in literature, resulting to optimum PCEs for PSC devices. However, correcting the iodide content into the sub-stoichiometric SA by adding 10% excess of PbI$_2$ during the fabrication of perovskite solar cells is accompanied by introduction of excess lead ions, resulting in accumulation of those lead ions into the perovskite grains or at the grain boundaries.
Figure 3.6: XRD patterns of CH$_3$NH$_3$PbI$_3$ micro-crystals synthesized using commercial sub-stoichiometric SA PbI$_2$ in reaction (a) with different amount of excess by weight of CH$_3$NH$_3$I (10 %, 15 %, 20 % and 25 %) and (b) with 20 % excess by weight of CH$_3$NH$_3$I at higher magnification. Asterisk marks indicate the XRD peak correspond to the unreacted PbI$_2$ with Miller indices (001). XRD peaks with Miller indices (200) and (110) correspond to the perovskite with tetragonal crystal structure.

Whereas, the XRD spectra of the corresponding synthesised CH$_3$NH$_3$PbI$_3$ micro-crystals after the reaction of the almost stoichiometrically corrected in iodide MC2 with an excess by weight of CH$_3$NH$_3$I (2 %, 4 % and 6 %) for 24 hours at constant temperature of 90 °C, are shown in figure 3.7 a and 3.7 b. When 4 % excess by weight of CH$_3$NH$_3$I amount was used in reaction with the almost stoichiometric MC2 PbI$_2$ powder, this resulted in an even weaker XRD peak at diffracted angle 2θ = 12.74° that corresponds to unreacted PbI$_2$ and annotated with asterisk, as shown in figure 3.7 b. The stoichiometric ratios between the lead and iodide for the SA and MC2 PbI$_2$ powders, were calculated based on the need of 20 % more by weight amount of CH$_3$NH$_3$I reacting with the sub-stoichiometric SA or a 4 % excess by weight amount of CH$_3$NH$_3$I reacting with the almost stoichiometric MC2, for an approximate elimination of the XRD signal that corresponds to unreacted PbI$_2$ present in the CH$_3$NH$_3$PbI$_3$ micro-crystals. Subsequently, the lead to iodide ratio for the sub-stoichiometric SA and the almost stoichiometric MC2 were determined, based on the following analysis.
Figure 3.7: XRD patterns of CH$_3$NH$_3$PbI$_3$ micro-crystals synthesized using almost stoichiometric MC2 PbI$_2$ in reaction (a) with different amount of excess CH$_3$NH$_3$I by weight (2 %, 4 % and 6 %) and (b) with 4 % of excess CH$_3$NH$_3$I by weight at higher magnification. Asterisk marks indicate the XRD peak correspond to the unreacted PbI$_2$ with Miller indices (001). XRD peaks with Miller indices (200) and (110) correspond to the perovskite with tetragonal crystal structure.
0.5 g of the sub-stoichiometric SA PbI\textsubscript{2} powder and an equimolar amount plus 20 % excess by weight of CH\textsubscript{3}NH\textsubscript{3}I (0.1724 g + 0.0345 g), were mixed in 15 mL of 1-pentanol and stirred for 24 hours at constant temperature of 90 °C. The mass of the sub-stoichiometric SA PbI\textsubscript{2} powder might vary, however proportionally 20 % excess by weight of CH\textsubscript{3}NH\textsubscript{3}I, must be added. The excess added mass of CH\textsubscript{3}NH\textsubscript{3}I which is 0.0345 g contains 0.0069 g of CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+}, corresponding to the summation of the atomic mass units of the elements present in CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+}, which for carbon is 12.0107 a.m.u., hydrogen 1.0079 a.m.u. and nitrogen 14.0067 a.m.u. While the remaining 0.0276 g correspond to the mass of I\textsuperscript{-} (iodide) with atomic mass unit of 126.9045 a.m.u. Based on the previous parameters, in order for the 0.5 g of the sub-stoichiometric SA PbI\textsubscript{2} powder be stoichiometrically correct, it should contain an extra mass of iodide that corresponds to 0.0276 g. The corrected in iodide sub-stoichiometric SA PbI\textsubscript{2}, with mass 0.5276 g (0.5 g + 0.0276 g), now is used for determination of its actual stoichiometry. Considering first the number of PbI\textsubscript{2} molecules were calculated after dividing the new corrected weight of PbI\textsubscript{2} (0.5276 g) with the molecular weight of PbI\textsubscript{2} (461.01 g * mol\textsuperscript{-1}) and multiplying by the Avogadro constant (6.022 * 10\textsuperscript{23} molecules * mol\textsuperscript{-1}), resulting in 6.8918 * 10\textsuperscript{20} being the number of PbI\textsubscript{2} molecules. However, in each of these PbI\textsubscript{2} molecules there are 3 atoms (1 lead atom and 2 iodide atoms), resulting in 20.6754 * 10\textsuperscript{20} of atoms in total. Proportionally the number of iodide present in PbI\textsubscript{2}, corresponds to 66.66 % of the total number of atoms (13.7836 * 10\textsuperscript{20}), while the remaining 33.33% are lead atoms (6.8918 * 10\textsuperscript{20} atoms). Also, the number of iodide atoms originating from the excess CH\textsubscript{3}NH\textsubscript{3}I was calculated by dividing the mass of excess iodide added (0.0276 g) with the molecular weight of elemental iodide (126.9045 g * mol\textsuperscript{-1}) and multiplying by the Avogadro constant (6.022 * 10\textsuperscript{23} atoms * mol\textsuperscript{-1}), resulting in 1.3097 * 10\textsuperscript{20} being the number of iodide atoms that are missing from the sub-stoichiometric SA PbI\textsubscript{2} powder. Consequently, the total number of iodide atoms actually present in the initially neat sub-stoichiometric SA PbI\textsubscript{2} was (12.4739 * 10\textsuperscript{20}), based on the correction of iodide content in PbI\textsubscript{2} occurring after adding 20 % excess by weight of CH\textsubscript{3}NH\textsubscript{3}I minus the iodide atoms added (13.7836 * 10\textsuperscript{20} - 1.3097 * 10\textsuperscript{20} = 12.4739 * 10\textsuperscript{20}). Therefore, the final ratio between the lead to iodide atoms in the sub-stoichiometric SA PbI\textsubscript{2} is 1: (12.4739 * 10\textsuperscript{20} / 6.8918 * 10\textsuperscript{20}) or 1 : 1.81. However, since a weak diffracted peak that corresponds to unreacted PbI\textsubscript{2} was detected during the synthesis of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals, as shown in figure 3.6 b, implies that the excess amount of CH\textsubscript{3}NH\textsubscript{3}I used should be slightly larger, perhaps
~21 – 22 % by weight for complete elimination of the unreacted PbI$_2$. For comparison, the calculated lead to iodide ratio for the sub-stoichiometric SA is 1 : 1.79, when 22 % excess by weight of CH$_3$NH$_3$I was used. The same retrospective methodology was followed when the almost stoichiometric MC2 PbI$_2$ powder used in reaction with 4 % excess by weight of CH$_3$NH$_3$I, during the synthesis of CH$_3$NH$_3$PbI$_3$ micro-crystals, results in a ratio between the lead to iodide atoms to be 1 : 1.96.

To understand the presence and formation of unreacted PbI$_2$ into the CH$_3$NH$_3$PbI$_3$ when sub-stoichiometric PbI$_2$ is used, the following theory was developed:

Since the general chemical formula of perovskite is ABX$_3$, that requires the presence of 3 halogen atoms. Specifically, in CH$_3$NH$_3$PbI$_3$ two iodide atoms originated from the PbI$_2$ while one iodide atom originated from CH$_3$NH$_3$I. That requires both reactants (PbI$_2$ and CH$_3$NH$_3$I) being stoichiometrically perfect. However, when sub-stoichiometric PbI$_2$ is used, its correct chemical formula must be written as Pb$_x$I$_2$ with $x < 2$. The percentage of unreacted PbI$_2$ into the CH$_3$NH$_3$PbI$_3$ when sub-stoichiometric Pb$_x$I is used could be calculated from mathematical equation 3.1:

$$\left(1 - \left(\frac{x}{2}\right)\right) \times 2 \times 100\%$$  

Mathematical equation 3.1

In which, $x$ is the number of iodide ions into the initially sub-stoichiometric Pb$_x$I used, $(1 - (x \div 2)) \times 100\%$ is the percentage of iodide missing from the initially sub-stoichiometric Pb$_x$I used and 2 is the number of iodide ions that needed for the formation of unreacted PbI$_2$. Also, we accept the condition that unreacted PbI$_2$ is again stoichiometrically perfect and not sub-stoichiometric, otherwise if the unreacted PbI$_2$ is sub-stoichiometric then its amount into the CH$_3$NH$_3$PbI$_3$ is even higher. To examine that approach a few examples are provided in table 3.5. Based on the previous analysis, initially more iodide is missing from the sub-stoichiometric Pb$_x$I used towards the synthesis of CH$_3$NH$_3$PbI$_3$ higher the amount of unreacted PbI$_2$. Also, similar trend is calculated for the remaining CH$_3$NH$_3^+$ ions that do not participate at the chemical reaction.
<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>( \text{PbI}_{1.65} + \text{CH}_3\text{NH}_3\text{I} )</th>
<th>( \text{PbI}_{1.92} + \text{CH}_3\text{NH}_3\text{I} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of ions</td>
<td>( 1 \text{ Pb}^+ )</td>
<td>( 1 \text{ Pb}^+ )</td>
</tr>
<tr>
<td></td>
<td>( 1 \text{ CH}_3\text{NH}_3^+ )</td>
<td>( 1 \text{ CH}_3\text{NH}_3^+ )</td>
</tr>
<tr>
<td></td>
<td>( 2.65 \text{ I}^- )</td>
<td>( 2.92 \text{ I}^- )</td>
</tr>
<tr>
<td>Total number of ions forming the ( \text{CH}_3\text{NH}_3\text{PbI}_3 )</td>
<td>( 0.65 \text{ Pb}^+ )</td>
<td>( 0.92 \text{ Pb}^+ )</td>
</tr>
<tr>
<td></td>
<td>( 0.65 \text{ CH}_3\text{NH}_3^+ )</td>
<td>( 0.92 \text{ CH}_3\text{NH}_3^+ )</td>
</tr>
<tr>
<td></td>
<td>( 1.95 \text{ I}^- )</td>
<td>( 2.76 \text{ I}^- )</td>
</tr>
<tr>
<td></td>
<td>or ( (0.65 \text{ CH}_3\text{NH}_3\text{PbI}_3) )</td>
<td>or ( (0.92 \text{ CH}_3\text{NH}_3\text{PbI}_3) )</td>
</tr>
<tr>
<td>Total number of ions for unreacted ( \text{PbI}_2 )</td>
<td>( 0.35 \text{ Pb}^+ )</td>
<td>( 0.08 \text{ Pb}^+ )</td>
</tr>
<tr>
<td></td>
<td>( 0.7 \text{ I}^- )</td>
<td>( 0.16 \text{ I}^- )</td>
</tr>
<tr>
<td></td>
<td>or ( (0.35 \text{ PbI}_2) )</td>
<td>or ( (0.08 \text{ PbI}_2) )</td>
</tr>
<tr>
<td>Total number of ( \text{CH}_3\text{NH}_3^+ ) ions</td>
<td>( 0.35 \text{ CH}_3\text{NH}_3^+ )</td>
<td>( 0.08 \text{ CH}_3\text{NH}_3^+ )</td>
</tr>
</tbody>
</table>

Table 3.5: Examples of chemical reactions between sub-stoichiometric \( \text{PbI}_x \) and \( \text{CH}_3\text{NH}_3\text{I} \) towards the formation of \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) and resulted unreacted \( \text{PbI}_2 \) and \( \text{CH}_3\text{NH}_3^+ \) ions.

3.2.6 Through lens detector-SEM spectra of \( \text{PbI}_2 \)

In order to qualify the influence of variability in the stoichiometry and polytypism between the sub-stoichiometric SA \( \text{PbI}_2 \) crystallised in a single polytypic phase and the almost stoichiometric MC2 \( \text{PbI}_2 \) crystallised in more than one polytypic phases, spectra of secondary electrons (SE) were collected from \( \text{PbI}_2 \) pellets using a through lens detector in scanning electron microscope (TLD-SEM). The differentiated intensity
of the SE as function of their deflected energy, indicated significant energy difference in the work function ($\Phi$) between the sub-stoichiometric SA and the almost stoichiometric MC2 PbI$_2$, as shown in figure 3.8. That may be attributed to the presence of more than one polytypic phase present in the almost stoichiometric MC2 PbI$_2$. This results in displacement of the Fermi energy closer to the conduction band, since the differentiated intensity of the SE is more enhanced for the almost stoichiometric MC2 PbI$_2$.

![Differentiated intensity spectra of the SE as function of their deflected energy from pellets made of the sub-stoichiometric SA or the almost stoichiometric MC2 PbI$_2$. $\Phi$ represents the work function.](image)

**Figure 3.8:** Differentiated intensity spectra of the SE as function of their deflected energy from pellets made of the sub-stoichiometric SA or the almost stoichiometric MC2 PbI$_2$. $\Phi$ represents the work function.

### 3.2.7 Implications of stoichiometry and polytypism of PbI$_2$ used to fabricate perovskite

The importance of stoichiometry and polytypism has been studied by comparing the sub-stoichiometric SA crystallised in a single polytypic phase and the almost stoichiometric MC2 crystallised in more than one polytypic phase PbI$_2$ powders used to fabricate CH$_3$NH$_3$PbI$_3$. The method of synthesis 1-pentanol / PbI$_2$ / CH$_3$NH$_3$I, similar
to Acik et al.,\textsuperscript{20} was used in the preparation of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals, followed by XRD characterisation. The CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals were prepared at range of temperatures (20 °C, 50 °C, 70 °C and 90 °C) and over a constant time of 24 hours. With regards to the PbI\textsubscript{2} used and the amount of CH\textsubscript{3}NH\textsubscript{3}I, samples were categorised into two groups. In the first group, mechanochemical almost stoichiometric MC2 PbI\textsubscript{2} powder reacted with a) an equimolar amount of CH\textsubscript{3}NH\textsubscript{3}I or b) an excess of CH\textsubscript{3}NH\textsubscript{3}I (30% more CH\textsubscript{3}NH\textsubscript{3}I by weight) followed by XRD characterisation, as shown in figures 3.9 a and 3.9 b, respectively. Whereas, in the second group, sub-stoichiometric SA PbI\textsubscript{2} powder reacted with c) an equimolar amount of CH\textsubscript{3}NH\textsubscript{3}I or d) an excess of CH\textsubscript{3}NH\textsubscript{3}I (30% more CH\textsubscript{3}NH\textsubscript{3}I by weight), followed by XRD characterisation, as shown in figures 3.9 c and 3.9 d, respectively.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{XRD patterns for CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals prepared at different temperatures.}
\end{figure}
Figure 3.9: XRD patterns of the CH$_3$NH$_3$PbI$_3$ micro-crystals synthesised at different temperatures and using different PbI$_2$ samples (asterisks correspond to the XRD peaks of the lead iodide). (a) mechanochemical MC2 and equimolar CH$_3$NH$_3$I, (b) mechanochemical MC2 and equimolar CH$_3$NH$_3$I plus 30% by weight of CH$_3$NH$_3$I, (c) commercial SA and equimolar CH$_3$NH$_3$I, (d) commercial SA and equimolar CH$_3$NH$_3$I plus 30% by weight of CH$_3$NH$_3$I. Normalization of XRD patterns, was in respect to (110) peak that corresponds to CH$_3$NH$_3$PbI$_3$ with tetragonal crystal structure in all patterns, except from that of (c) commercial SA and equimolar CH$_3$NH$_3$I at 20 °C, which is in respect to the peak of the lead iodide (001).

When equimolar amounts of reactants were used in the synthesis of the CH$_3$NH$_3$PbI$_3$ micro-crystals, an XRD peak at the diffraction angle 2θ = 12.74° that corresponds to unreacted PbI$_2$ (annotated with an asterisk) was detected. Also, that diffraction peak was less strong when the almost stoichiometric MC2 instead of the sub-stoichiometric SA PbI$_2$ powders were used. The percentage of the unreacted PbI$_2$ present in the powder of the CH$_3$NH$_3$PbI$_3$ micro-crystals after each reaction at each temperature was calculated based on the relative integrated area under the primary XRD peak at the diffraction angle 2θ = 12.74° of PbI$_2$ with Miller indices (001), with respect to the integrated area under the pair of XRD peaks at diffraction angles 2θ = 14.1° and 2θ = 14.2° that correspond to the CH$_3$NH$_3$PbI$_3$ with tetragonal crystal structure and planes
with Miller indices (200) and (110), as summarized in table 3.6. It was noted that, the 52.5 % of unreacted PbI$_2$ powder yellow in colour, was easily observed during the filtration process of CH$_3$NH$_3$PbI$_3$ micro-crystal powder synthesised using equimolar amounts of the sub-stoichiometric SA PbI$_2$ and CH$_3$NH$_3$I under constant temperature of 20 ºC, as shown in figure 3.10.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>MC2 / CH$_3$NH$_3$I equimolar</th>
<th>SA / CH$_3$NH$_3$I equimolar</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>14.5</td>
<td>52.5</td>
</tr>
<tr>
<td>50</td>
<td>3.1</td>
<td>10.9</td>
</tr>
<tr>
<td>70</td>
<td>4.5</td>
<td>11.4</td>
</tr>
<tr>
<td>90</td>
<td>3.9</td>
<td>15.7</td>
</tr>
</tbody>
</table>

Table 3.6: Percentage of the unreacted PbI$_2$ present in CH$_3$NH$_3$PbI$_3$ micro-crystals, as function of the temperature and source of PbI$_2$.

Figure 3.10: Unreacted PbI$_2$ powder (yellow colour) in the synthesised powder of the CH$_3$NH$_3$PbI$_3$ micro-crystals synthesised using equimolar amounts of the sub-stoichiometric SA PbI$_2$ and CH$_3$NH$_3$I under a constant temperature of 20 ºC for 24 hours, scale bar represents 10 mm.
The varying percentage of unreacted PbI₂ present into the CH₃NH₃PbI₃ micro-crystals powders synthesised using equimolar amounts of either the sub-stoichiometric SA or almost stoichiometric MC2 PbI₂ with CH₃NH₃I, indicates the stoichiometric deviation from the optimum ratio between the lead and iodide atoms present in the PbI₂. We assume, when equimolar amounts of either the sub-stoichiometric or the almost stoichiometric MC2 PbI₂ and CH₃NH₃I react together, the concentration of iodide anions (I⁻) originating from the CH₃NH₃I were not adequate to fulfil the formation of the CH₃NH₃PbI₃ and resulted in some unreacted PbI₂. This is consistent with the reported incorporation of hydroiodic acid (HI) sometimes used as an additive, during the formation of CH₃NH₃PbI₃ for improved device performance, resulting in a correction of the iodide content in the PbI₂. In contrast, when a 30% excess by weight of CH₃NH₃I was added during the synthesis of the CH₃NH₃PbI₃ micro-crystals at temperatures above 50 °C, zero amount of unreacted PbI₂ was detected by XRD, regardless of the PbI₂ source used (either almost stoichiometric MC2 or sub-stoichiometric SA). Additionally, only minor differences were observed in the XRD spectra of the CH₃NH₃PbI₃ micro-crystals synthesised above 50 °C, related to the number of different polytypic phases present in either the almost stoichiometric MC2 or sub-stoichiometric SA PbI₂, as shown in figures 3.9 b and 3.9 d, respectively. In figures 3.9 b and 3.9 d, nine XRD peaks correspond to unreacted PbI₂ crystallised in different polytypic phases, as indicated with asterisks. These were detected after the synthesis of CH₃NH₃PbI₃ micro-crystals at a temperature of 20 °C using the almost stoichiometric MC2 PbI₂. Whereas, only five XRD peaks corresponding to unreacted PbI₂ crystallised in a single polytypic phase, as indicated with asterisks, were detected after the synthesis of CH₃NH₃PbI₃ micro-crystals at 20 °C using the sub-stoichiometric SA PbI₂. Consequently, the number of different polytypic phases present in the PbI₂, does not affect the formation of perovskite. However, in contrast the stoichiometric ratio between the lead to iodide in the PbI₂ used does affect the formation of perovskite.

3.2.8 Morphology of perovskite thin films

Morphological characterisation of the CH₃NH₃PbI₃ thin films fabricated either by CH₃NH₃PbI₃ micro-crystals or equimolar amounts of PbI₂ with CH₃NH₃I, indicates the formation of two-dimensional CH₃NH₃PbI₃ layered structures independent of the stoichiometric variability in the PbI₂ used. These layered structures have also been
noted in literature\textsuperscript{22–24} and were confirmed by atomic force microscopy (AFM) and through lens detector scanning electron microscopy (TLD-SEM) images, as shown in figures 3.11 and 3.12, respectively. Random orientation of those layered structures, accompanied by the presence of unreacted PbI\textsubscript{2}, may provide an explanation for the spatial variability of the $J_{SC}$ within individual CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} grains reported in the literature.\textsuperscript{25} Furthermore, spatial interconnections between the individual grains containing two dimensional layered structures were observed, when the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films were fabricated from either CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals regardless of the PbI\textsubscript{2} used (sub-stoichiometric SA or almost stoichiometric MC2) or by reacting equimolar amounts of the almost stoichiometric MC2 PbI\textsubscript{2} with CH\textsubscript{3}NH\textsubscript{3}I. In contrast, when the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films fabricated by reacting equimolar amounts of the sub-stoichiometric SA PbI\textsubscript{2} with CH\textsubscript{3}NH\textsubscript{3}I, reduced spatial interconnection between individual grains containing the two-dimensional layered structures was noticed. The grains in figures 3.11 d and 3.12 d have more distinct boundaries than the grains in all the other corresponding images. The measured roughness of all fabricated CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films using the vacuum assisted method was less than 16 nm, as measured by AFM. Also, an increased concentration of formed voids on top of the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films fabricated by the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals regardless of the PbI\textsubscript{2} used (sub-stoichiometric SA or almost stoichiometric MC2) as observed in TLD-SEM images 3.12 a and 3.12 b, might originate from the low concentration (1.13 M) of the dissolved CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals in dry DMSO. Also, through all the TLD-SEM images in figure 3.12, grain size distribution calculations were summarized as shown in figure 3.13. Specifically, the majority of grains in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films had an average size of 110 ± 10 nm when CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals employed and fabricated using the almost stoichiometric MC2 PbI\textsubscript{2}. Whereas the majority of grains had an average size of 90 ± 10 nm when CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals used which made using the sub-stoichiometric SA PbI\textsubscript{2}. However, equimolar amounts of the almost stoichiometric MC2 PbI\textsubscript{2} / CH\textsubscript{3}NH\textsubscript{3}I results in thin films with maximum average grain size 175 ± 25 nm. Simultaneously, thin films of perovskite made of equimolar amounts of sub-stoichiometric SA PbI\textsubscript{2} / CH\textsubscript{3}NH\textsubscript{3}I shown an average grain size of 130 ± 10 nm. Obviously, a different growth mechanism in perovskite thin films is applied between the use of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} micro-crystals and equimolar amounts of reactants, which requires further investigation.
Figure 3.11: AFM images of CH$_3$NH$_3$PbI$_3$ thin films fabricated using, (a) CH$_3$NH$_3$PbI$_3$ micro-crystals made using almost stoichiometric MC2 PbI$_2$, (b) CH$_3$NH$_3$PbI$_3$ micro-crystals made using sub-stoichiometric SA PbI$_2$, (c) equimolar amounts of almost stoichiometric MC2 PbI$_2$ / CH$_3$NH$_3$I, (d) equimolar amounts of sub-stoichiometric SA PbI$_2$ / CH$_3$NH$_3$I. The average values of roughness, are listed below at each image.
Figure 3.12: Low voltage through lens detector scanning electron microscope (TLD - SEM) images of CH$_3$NH$_3$PbI$_3$ thin films fabricated using, (a) CH$_3$NH$_3$PbI$_3$ micro-crystals made using almost stoichiometric MC2 PbI$_2$, (b) CH$_3$NH$_3$PbI$_3$ micro-crystals made using sub-stoichiometric SA PbI$_2$, (c) equimolar amounts of almost stoichiometric MC2 PbI$_2$/CH$_3$NH$_3$I and (d) equimolar amounts of sub-stoichiometric SA PbI$_2$/CH$_3$NH$_3$I. Two dimensional layered structures of CH$_3$NH$_3$PbI$_3$ into grains, are indicated with blue arrows in all images, while unreacted PbI$_2$ is indicated with green arrows. Scale bars represent 1 μm.
3.2.9 Vis-IR spectra of perovskite thin films as function of the PbI$_2$ used

The presence of unreacted PbI$_2$ either between or within the grains of the CH$_3$NH$_3$PbI$_3$ thin films fabricated using equimolar amounts of the sub-stoichiometric SA PbI$_2$ in reaction with CH$_3$NH$_3$I, was confirmed by the strong absorption observed around ~530 nm, as shown in the visible-infrared (Vis-IR) spectra in figure 3.14. The optical band gap values ($E_{\text{obg}}$) of the unreacted PbI$_2$ present ($E_{\text{obg}}=2.34$ eV ($\pm 0.02$ eV) was calculated based on five measurements, while the optical band gap related to the CH$_3$NH$_3$PbI$_3$ ($E_{\text{obg}}=1.48$ eV) for the thin films fabricated using equimolar amounts of the sub-stoichiometric SA PbI$_2$ in reaction with CH$_3$NH$_3$I. The relevant Tauc plots, are shown in figures 3.15 and 3.16. The hypothesis that unreacted PbI$_2$ might be present within the perovskite grains, is supported by the values of the optical band gaps that correspond to the neat PbI$_2$ ($E_{\text{obg}}=2.36$ eV) and the CH$_3$NH$_3$PbI$_3$ ($E_{\text{obg}}=1.51$ eV),$^{26}$ as shown in figures 3.15 and 3.16, respectively. It is assumed, that in the CH$_3$NH$_3$PbI$_3$ thin films fabricated using equimolar amounts of the sub-stoichiometric SA PbI$_2$ in reaction with CH$_3$NH$_3$I, the amount of iodide present in the sub-stoichiometric SA PbI$_2$, 

![Figure 3.13: Grain size distribution of CH$_3$NH$_3$PbI$_3$ thin films (based on TLD - SEM images) fabricated using, (a) CH$_3$NH$_3$PbI$_3$ micro-crystals made using almost stoichiometric MC2 PbI$_2$, (b) CH$_3$NH$_3$PbI$_3$ micro-crystals made using sub-stoichiometric SA PbI$_2$, (c) equimolar amounts of almost stoichiometric MC2 PbI$_2$/CH$_3$NH$_3$I and (d) equimolar amounts of sub-stoichiometric SA PbI$_2$/CH$_3$NH$_3$I.](image)
is insufficient to form a continuous composition of the CH$_3$NH$_3$PbI$_3$. This results in the formation of zones that are sufficiently iodide enriched (~ at least three iodide ions) and other zones that are depleted of iodide (less than three iodide ions).$^{27}$ Unreacted PbI$_2$ is formed in the depleted zones, while CH$_3$NH$_3$PbI$_3$ is formed in the enriched zones within the perovskite grains, respectively.

![Absorbance vs Wavelength](image)

**Figure 3.14:** Visible-infrared (Vis-IR) absorption spectra of perovskite thin films synthesised from, CH$_3$NH$_3$PbI$_3$ micro-crystals (using almost stoichiometric MC2 PbI$_2$) (black curve), CH$_3$NH$_3$PbI$_3$ micro-crystals (using sub-stoichiometric SA PbI$_2$) (red curve), equimolar amounts of almost stoichiometric MC2 PbI$_2$ / CH$_3$NH$_3$I (green curve) and equimolar amounts of sub-stoichiometric SA PbI$_2$ / CH$_3$NH$_3$I (blue curves from five different measurements). Strong absorption at ~ 530 nm corresponds to unreacted PbI$_2$ as indicated with black arrow.
Figure 3.15: Tauc plots of perovskite thin films synthesised from, \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) micro-crystals (using almost stoichiometric \( \text{MC}_2\text{PbI}_2 \) (black curve), \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) micro-crystals (using sub-stoichiometric SA \( \text{PbI}_2 \) (red curve), equimolar amounts of almost stoichiometric \( \text{MC}_2\text{PbI}_2 / \text{CH}_3\text{NH}_3\text{I} \) (green curve) and equimolar amounts of sub-stoichiometric SA \( \text{PbI}_2 / \text{CH}_3\text{NH}_3\text{I} \) (blue curves from five different measurements).

Figure 3.16: Tauc plots of perovskite thin films synthesised from, \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) micro-crystals (using almost stoichiometric \( \text{MC}_2\text{PbI}_2 \) (black curve), \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) micro-crystals (using sub-stoichiometric SA \( \text{PbI}_2 \) (red curve), equimolar amounts of almost stoichiometric \( \text{MC}_2\text{PbI}_2 / \text{CH}_3\text{NH}_3\text{I} \) (green curve) and equimolar amounts of sub-stoichiometric SA \( \text{PbI}_2 / \text{CH}_3\text{NH}_3\text{I} \) (blue curves from five different measurements). The \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) optical band gaps (\( \sim 1.51 \text{eV} \)) are indicated with black / red / green arrows. \( \text{CH}_3\text{NH}_3\text{PbI}_3 / \text{PbI}_2 \) optical band gap (\( \sim 1.48 \text{eV} \)) is indicated with blue arrow.
3.2.10 The importance of the stoichiometry in PbI$_2$ used to produce perovskite solar cells

Perovskite solar cell (PSC) devices with regular (n – i – p) architecture were fabricated with the stacking sequence: glass / ITO / SnO$_2$ / CH$_3$NH$_3$PbI$_3$ / Spiro-MeOTAD / Au, in order to determine the importance of the variable stoichiometry and polytypism present in the PbI$_2$ used. Deposition of all the CH$_3$NH$_3$PbI$_3$ photoactive layers present was accomplished using the same vacuum assisted method, as described in experimental methods (chapter 2) and shown in figures 3.17 a and 3.17 b. The vacuum applied accelerates the extraction of dry DMSO solvent in a single step without any antisolvent rinsing process. One set of PSCs devices were fabricated by dissolving either the sub-stoichiometric SA or the almost stoichiometric MC2 PbI$_2$ powders, with equimolar amounts of CH$_3$NH$_3$I in dry DMSO, results in photoactive thin films with thicknesses ~ 350 nm (± 10 nm), as determined by atomic force microscopy (AFM). A second set of PSC devices was fabricated by re-dissolving the corresponding CH$_3$NH$_3$PbI$_3$ micro-crystals in dry DMSO (synthesised as described below), results in photoactive thin films with thicknesses ~ 300 nm (± 10 nm), as determined by atomic force microscopy (AFM).

Figure 3.17: Images of glass / ITO / SnO$_2$ / perovskite after (a) extracting the dry DMSO under vacuum for 120 s before annealing and (b) after annealing at 100 °C for 30 s, scale bars represent 10 mm. (Corresponding marks near the edges of sample in figure (b) are made by tweezers).
CH$_3$NH$_3$PbI$_3$ micro-crystals were synthesised at a temperature of 90 °C using either the sub-stoichiometric SA or the almost stoichiometric MC2 PbI$_2$ powders in reaction with a 30 % excess by weight of CH$_3$NH$_3$I. Minor differences were observed in the morphology of the CH$_3$NH$_3$PbI$_3$ micro-crystals as observed by scanning electron microscopy (SEM) images, as shown in figures 3.18 a and 3.18 b.

![SEM images](image_url)

**Figure 3.18**: Scanning electron microscopy (SEM) images of CH$_3$NH$_3$PbI$_3$ micro-crystals synthesised at temperature 90 °C, using (a) the almost stoichiometric mechanochemical MC 2 or (b) the sub-stoichiometric SA PbI$_2$ powders in reaction with a 30% more by weight of CH$_3$NH$_3$I, scale bars represent 10μm.
The average and champion photovoltaic parameters (Fill Factor (FF), short circuit current ($J_{SC}$), open circuit voltage ($V_{OC}$) and power conversion efficiency (PCE)), of the PSCs were measured during a reverse scan ($V_{OC} \rightarrow 0$) with a scan step of 100 mV, are listed in Table 3.7 and illustrated graphically in Figure 3.19. Also, the characteristic current density – voltage curves in forward (0 → $V_{OC}$) and reverse ($V_{OC} \rightarrow 0$) scans of PSC devices with structure glass / ITO / SnO$_2$/ CH$_3$NH$_3$Pbl$_3$ / Spiro-MeOTAD / Au, as a function of the photoactive layer fabricated using either CH$_3$NH$_3$Pbl$_3$ micro-crystals or equimolar amounts of different PbI$_2$ with CH$_3$NH$_3$I, are shown in Figure 3.20. In all the following plots, black curves correspond to the average of all current density – voltage curves recorded and the coloured stripes represent the deviation between each initially recorded current density – voltage curve from the black curve. Green coloured stripes that represent the measurements of fresh PSCs.

<table>
<thead>
<tr>
<th>Dissolution of CH$_3$NH$_3$Pbl$_3$ micro-crystals in DMSO</th>
<th>FF (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (Volts)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NH$_3$Pbl$_3$ micro-crystals (synthesised using MC2 PbI$_2$)</td>
<td>68.19 (73.66)</td>
<td>20.98 (21.61)</td>
<td>1.03 (1.04)</td>
<td>14.69 (16.55)</td>
</tr>
<tr>
<td>CH$_3$NH$_3$Pbl$_3$ micro-crystals (synthesised using SA PbI$_2$)</td>
<td>72.08 (75.82)</td>
<td>20.87 (21.65)</td>
<td>1.06 (1.06)</td>
<td>16.02 (17.40)</td>
</tr>
<tr>
<td>Dissolution of equimolar PbI$_2$/ CH$_3$NH$_3$I in DMSO</td>
<td>FF (%)</td>
<td>$J_{SC}$ (mA/cm$^2$)</td>
<td>$V_{OC}$ (Volts)</td>
<td>PCE (%)</td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
<td>--------</td>
<td>---------------------</td>
<td>------------------</td>
<td>---------</td>
</tr>
<tr>
<td>MC2 PbI$_2$/ CH$_3$NH$_3$I (equimolar)</td>
<td>71.75 (75.29)</td>
<td>21.09 (21.60)</td>
<td>1.04 (1.05)</td>
<td>15.77 (17.07)</td>
</tr>
<tr>
<td>SA PbI$_2$/ CH$_3$NH$_3$I (equimolar)</td>
<td>34.18 (41.01)</td>
<td>13.06 (14.96)</td>
<td>1.02 (1.02)</td>
<td>4.58 (6.26)</td>
</tr>
</tbody>
</table>

Table 3.7: The Fill Factor (FF), short circuit current ($J_{SC}$), open circuit voltage ($V_{OC}$) and power conversion efficiency (PCE)) of PSCs devices with structure glass / ITO / SnO$_2$/ CH$_3$NH$_3$Pbl$_3$ / Spiro-OmeTAD / Au, as a function of the PbI$_2$ powder and the synthesised CH$_3$NH$_3$Pbl$_3$ micro-crystals used. The PSCs parameters correspond to the average values from 20 devices in bold and champion devices in parenthesis.
Figure 3.19: The Fill Factor (FF), short circuit current ($J_{sc}$), power conversion efficiency (PCE) and open circuit voltage ($V_{oc}$) of PSCs devices with structure glass / ITO / SnO$_2$ / CH$_3$NH$_3$PbI$_3$ / Spiro-OMeTAD / Au, as a function of the PbI$_2$ powder and the synthesised CH$_3$NH$_3$PbI$_3$ micro-crystals used.
Figure 3.20: Characteristic current density – voltage curves in forward (0 → V_{OC}) and reverse (V_{OC} → 0) scans of PSC devices with structure glass / ITO / SnO₂ / CH₃NH₃PbI₃ / Spiro - OMeTAD / Au, as function of the photoactive layer fabricated using either CH₃NH₃PbI₃ micro-crystals or equimolar amounts of different PbI₂ with CH₃NH₃I. (a) CH₃NH₃PbI₃ micro-crystals made using almost stoichiometric MC2 PbI₂, (b) CH₃NH₃PbI₃ micro-crystals made using sub-stoichiometric SA PbI₂, (c) equimolar amounts of almost stoichiometric MC2 PbI₂ / CH₃NH₃I and (d) equimolar amounts of sub-stoichiometric SA PbI₂ / CH₃NH₃I. Black curves correspond to the average of current density – voltage curves and coloured stripes to their deviation from the average black curve. Green and red coloured stripes, indicate current density – voltage data collected in forward (0 → V_{OC}) and reverse (V_{OC} → 0) scans, respectively.

The photovoltaic parameters (FF, V_{OC}, J_{SC} and PCE) of PSC devices were significantly enhanced, when the photoactive layer was fabricated by using either the re-dissolved CH₃NH₃PbI₃ micro-crystals or equimolar amounts of almost stoichiometric MC2 PbI₂ with CH₃NH₃I. Using the re-dissolved micro-crystals, will have the effect of correcting the iodide content in the used PbI₂ (both the sub-stoichiometric SA or almost stoichiometric MC2), because the micro-crystals were synthesised in a 30 % excess by weight of CH₃NH₃I. The almost stoichiometric MC2 PbI₂ had a closer to the identical lead to iodide ratio. In contrast, when the photoactive layer was fabricated by using equimolar amounts of the sub-stoichiometric SA PbI₂ in reaction with CH₃NH₃I, the photovoltaic parameters (FF, J_{SC} and PCE) of PSC devices were remarkably inferior.
That is reflected by the non-identical (1:2) atomic ratio between the lead to iodide in SA PbI₂ used and the presence of unreacted PbI₂, as analysed in the previous section (3.2.5 Determining the stoichiometry in PbI₂ by XRD). However, the values of $V_{OC}$ did not follow the similar inferior trend, indicating absence of shunt paths. The presence of unreacted PbI₂ either between or presumably within the grains of the CH₃NH₃PbI₃,²⁹–³¹ is responsible for charge carriers recombination which reduces the photocurrent and hinders device performance, when the CH₃NH₃PbI₃ thin film is fabricated using equimolar amounts of the sub-stoichiometric SA PbI₂ in reaction with CH₃NH₃I. Additionally, a debatable issue has been emerged around the role of the excess PbI₂ used and the presence of unreacted PbI₂ during the formation of perovskite as previously presented by Adachi et al., Dai et al., Seok et al. and Jacobsson et al.³,³²–³⁴ We believe that if sub-stoichiometric PbI₂ is used for the synthesis of perovskites as a first step, the content of halogen should be carefully corrected obeying to the general chemical formula for perovskites (ABX₃) in a repeatable way and as a further in parallel second step the excess of PbI₂ added to be correlated with optoelectronic properties of the final perovskite. Theoretically, the presence of added ions in a stoichiometrically perfect perovskite originated from the excess of PbI₂ used, will improve the optoelectronic properties of PSC devices due to improved charge carriers transportation between the grain boundaries, inner volume of grains and the interfaces ETL/perovskite – perovskite/HTL. However, the amount of excess PbI₂ used might have an upper limit, which above that acts as a hindering barrier for the stability of perovskite, as noted by Adachi et al.³²

### 3.3 Conclusion

In conclusion, the synthesis of PbI₂ by employing planetary ball milling is a low-cost, water-free and energy efficient (~ 31.3 watts per hour per gram) process to produce moderate quantities (≥ 40 grams per run and yield ~ 96 ± 0.5 %). This mechanochemical method, is able to regulate both the stoichiometry and polytypism of the resulting PbI₂, by varying the mechanochemical parameters of synthesis (revolutions per minute and time duration), as determined by XRD, XPS and RBS analysis. Stoichiometric ratio between the lead to iodide atoms of mechanochemical and commercial PbI₂ powders was also evaluated by controllable synthesis of
CH$_3$NH$_3$PbI$_3$ micro-crystals. Planetary ball milling synthesis might result in reduction of lead oxyiodide and lead iodide hydroxide compounds, in comparison with the solvothermal process, as determined by EDS-SEM and XPS analysis. This is due to the absence of water molecules in the planetary ball milling process. Also, further reduction of oxygen ~ 36 (± 10) % in mechanochemical PbI$_2$, is achievable by displacing the ambient air inside the ball milling jar with argon gas. PSC devices fabricated with CH$_3$NH$_3$PbI$_3$ thin films as photoactive layers manufactured using sub-stoichiometric PbI$_2$, showed reduction in their average performance from ~ 15.5 % to ~ 4.6 % due to the presence of unreacted PbI$_2$, unless additional iodide was introduced via an excess of CH$_3$NH$_3$I, during the fabrication of CH$_3$NH$_3$PbI$_3$ micro-crystals. Also, CH$_3$NH$_3$PbI$_3$ thin films were manufactured using only DMSO which is a non-toxic solvent. In combination with a single step vacuum assisted method, promotion of two-dimensional layered structures were formed, regardless of the stoichiometry and polytypic phase present in the PbI$_2$ used. We believe, that using materials with corrected stoichiometry, alongside a simple and repeatable deposition process for the fabrication of PSC devices, might hold the key to consistently achieving high efficiency and more stable PSC.

3.4 References


Chapter 4

Implications of dopant agents in perovskite (CH$_3$NH$_3$PbI$_3$)

4.1 Introduction

As presented in chapter 3, only the stoichiometric ratio between the lead and iodide atoms and not the number of polytypic phases present in the PbI$_2$ powder (either commercial or mechanochemical), has significant implications at the quality of the CH$_3$NH$_3$PbI$_3$ formed. The optoelectronic properties in perovskites (such as the energy band gap, improved charge carrier transport), are strongly influenced by the different cations and halogens used. $^1$ The concept of controllable doping might lead to reproducible synthesis of perovskites with optimum and repeatable optoelectronic properties, since the coexistence of different mixtures of A and X ions with variable effective ionic radius, require a specific ratio between them resulting in a minimum of distortion in the crystal structure of perovskites formatted. In this chapter further steps, which include controllable doping either of the A or X or A and X sites the implications in the crystal structure of CH$_3$NH$_3$PbI$_3$ with general chemical formula ABX$_3$ are considered. Also, will be described in detail the importance of controllable substitution of methylammonium with formamidinium cations and iodide with bromide anions. The optimum ratio between the different substituted ions in the CH$_3$NH$_3$PbI$_3$ crystal structure, was determined by the tetragonal to cubic crystal structure transition in synthesised micro-crystals, in respect to the amount of substituted ions, as observed by X-ray diffraction (XRD) spectra. Morphological characterisation of the doped perovskite micro - crystals as fabricated and when cast into thin films, was accomplished by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The results were compared, alongside the undoped CH$_3$NH$_3$PbI$_3$ micro-crystals and thin films. Fluctuations in the optical band gap values, were also observed
in respect to the selective substitution of different ions in the CH$_3$NH$_3$PbI$_3$ crystal structure, as determined by visible-infrared (Vis-IR) spectroscopy. Additionally, the power conversion efficiency (PCE) of the perovskite solar cells (PSCs) devices subsequently fabricated using the synthesised perovskites with controlled doping levels within the photoactive layers, were evaluated over 240 hours.

4.2 Results and discussion

4.2.1 X-ray diffraction analysis of doped CH$_3$NH$_3$PbI$_3$ micro-crystals

Doped CH$_3$NH$_3$PbI$_3$ micro-crystals were syntheisised by the method of 1-pentanol / PbI$_2$ / CH$_3$NH$_3$I$^+$ in reaction with various amounts of dopants, either CH$_3$NH$_3$Br or CH(NH$_2$)$_2$I or CH(NH$_2$)$_2$I and Br$_2$, at a temperature of 90 °C and for a fixed duration of 24 hours. The amount dopants were calculated based on the number of PbI$_2$ moles used. All versions of the micro-crystals were fabricated by using the almost stoichiometric MC2 PbI$_2$ mixed with an equimolar amount plus 10 % excess by weight of CH$_3$NH$_3$I in reaction with the dopants, followed by XRD characterisation. An excess 10 % by weight of CH$_3$NH$_3$I was used in all chemical reactions during the manufacture of doped CH$_3$NH$_3$PbI$_3$ micro-crystals, since the mechanochemically synthesised MC2 PbI$_2$ is deficient in iodide by a 4 % (see chapter 3). The first group of doped CH$_3$NH$_3$PbI$_3$ micro-crystals were fabricated with various amounts of CH$_3$NH$_3$Br. This resulted in an optimum percentage of ~ 40 % additional CH$_3$NH$_3$Br moles, as defined by the transition from tetragonal to cubic crystal structure. The transition was indicated in the high resolution XRD patterns when the 1$^{st}$, 2$^{nd}$ and 3$^{rd}$ high intensity sets of peaks with diffraction angles 2θ in the ranges 11 ° to 16 °, 27 ° to 30 ° and 30 ° to 33 °, respectively, as shown in figures 4.1 a, 4.1 b, 4.1 c and 4.1 d. Change from the sets of multiple peaks to single peak, is indicative of the tetragonal to cubic structure transition. Similar crystallographic structural transitions, have also been observed in mixed cation halide perovskite single crystals, as noted in literature. 3–5 For the 1$^{st}$ set of peaks, the reduction of the diffracted peak that corresponds to plane with Miller indices (200) at angle 2θ ≈ 14.06 °, was observed as function of the CH$_3$NH$_3$Br added. This is not immediately evident in figure 4.1 a, but is noticeable when shown at higher resolution in figure 4.1 b. Meanwhile for the 2$^{nd}$ and 3$^{rd}$ sets of peaks, similar reductions were noted for the diffracted peaks that correspond to planes with Miller indices (004)
and (222) at angles $2\theta \approx 28.26^\circ$ and $2\theta \approx 31.72^\circ$, as shown in figures 4.1 c and 4.1 d, respectively.\textsuperscript{6,7}
This peak reduced, as increased the amount of Br$^-$.

**1st set of peaks**

- Pure CH$_3$NH$_3$PbI$_3$
- Added moles of CH$_3$NH$_3$Br

**2nd set of peaks**

- Pure CH$_3$NH$_3$PbI$_3$
- Added moles of CH$_3$NH$_3$Br
Figure 4.1: XRD patterns of CH$_3$NH$_3$PbI$_3$ micro-crystals synthesized using almost stoichiometric MC2 PbI$_2$ in reaction with equimolar plus an excess 10 % by weight of CH$_3$NH$_3$I and controllably added amount of CH$_3$NH$_3$Br. (a) for diffracted angle 2θ from 9° to 55°, (b) 1st set of peaks for diffracted angle 2θ from 11° to 16°, (c) 2nd set of peaks for diffracted angle 2θ from 27° to 30° and (d) 3rd set of peaks for diffracted angle 2θ from 30° to 33°. XRD peaks that correspond to crystallographic planes with Miller indices (200) and (110), referred to the perovskite with tetragonal crystal structure. Normalization in all XRD patterns, was in respect to XRD peak that corresponds to crystallographic plane with Miller indices (110).

However, this transition from tetragonal to cubic crystal structure due to the various amount of CH$_3$NH$_3$Br added, revealed only the effects of doping with respect to the X site in the general chemical formula for perovskites ABX$_3$.

In the second group of doped CH$_3$NH$_3$PbI$_3$ micro-crystals fabricated, a various amount of CH(NH$_2$)$_2$I was used. Resulting in an optimum percentage ~ 14 % of CH(NH$_2$)$_2$I moles added, again defined by the transition in the crystal structure as indicated in the high resolution XRD patterns. The transitions of the same 1st, 2nd and 3rd sets of peaks, are shown in figures 4.2 a, 4.2 b, 4.2 c and 4.2 d, as function of the CH(NH$_2$)$_2$I added. For the 1st set of peaks, the reduction of the diffraction peak that corresponds to the
(200) plane at angle $2\theta \approx 14.06^\circ$, was observed and shown in figure 4.2 b. While for the 2nd and 3rd sets of peaks, a decrease in the intensity of the diffracted peaks correspond to planes with Miller indices (004) and (222) at angles $2\theta \approx 28.26^\circ$ and $2\theta \approx 31.72^\circ$, was noted and shown in figures 4.2 c and 4.2 d, respectively. Also, when an excess amount of CH(NH$_2$)$_2$I added (> 14 % moles), distortion of the crystal structure of the already doped CH$_3$NH$_3$PbI$_3$, resulted in the reappearance of peaks on the higher angle side of the main diffracted peaks that correspond to (220) and (310) planes at angles $2\theta \approx 28.52^\circ$ and $2\theta \approx 31.94^\circ$, as shown in figure 4.2 c and 4.2 d, respectively. This is possibly related with a transition from cubic back to tetragonal crystal structure with different d spacing.
This peak reduced, as increased the amount of FA$^+$

Transition from tetragonal to cubic structure

This peak increased, as increased the amount of FA$^+$
Figure 4.2: XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ micro-crystals synthesized using almost stoichiometric MC2 PbI$_2$ in reaction with equimolar plus an excess 10% by weight of CH$_3$NH$_3$I and controllably added amount of CH(NH$_2$)$_2$I. (a) for diffracted angle 2$\theta$ from 9° to 55°, (b) 1$^{st}$ set of peaks for diffracted angle 2$\theta$ from 11° to 16°, (c) 2$^{nd}$ set of peaks for diffracted angle 2$\theta$ from 27° to 30° and (d) 3$^{rd}$ set of peaks for diffracted angle 2$\theta$ from 30° to 33°. XRD peaks that correspond to crystallographic planes with Miller indices (200) and (110), referred to the perovskite with tetragonal crystal structure. Normalization in all XRD patterns, was in respect to XRD peak that corresponds to crystallographic plane with Miller indices (110).

Nevertheless, the optimum amount of added CH(NH$_2$)$_2$I (~14% moles), caused a transition from tetragonal to cubic crystal structure, due to the doping at the A site. Consequently, the implication of a second transition at the crystal structure should be identified by a controllably introduced amount of bromide ions in X site, as previously reported by Eperon et al. 9

The third group of doped CH$_3$NH$_3$PbI$_3$ micro-crystals were doped with both CH(NH$_2$)$_2$I and Br$_2$, acting on the A and X sites in ABX$_3$, respectively. In this case the CH(NH$_2$)$_2$I doping was fixed at ~14% moles, and amount of Br$_2$ added was varied. The optimum amount of Br$_2$ used, was found to be ~10% moles, as determined based on the
transitions observed in the same set of XRD peaks (1\textsuperscript{st}, 2\textsuperscript{nd} and 3\textsuperscript{rd} sets of peaks with the highest intensity of diffraction at 2θ angle from 11° to 16°, 27° to 30° and 30° to 33°, respectively), as shown in figures 4.3 a, 4.3 b, 4.3 c and 4.3 d.
(b) Normalized counts (a.u.)
2-theta (degrees)
1st set of peaks
Added moles of Br$_2$
5 %
10 %
15 %
20 %
(110)

(c) Normalized counts (a.u.)
2-theta (degrees)
2nd set of peaks
Added moles of Br$_2$
5 %
10 %
15 %
20 %
(220)
From the 1st set of peaks, no significant change was observed at the diffracted peak that corresponds to plane with Miller indices (110) at angle $\theta \approx 14.18^\circ$ as a function of the Br$_2$ added and shown in figure 4.3 b. However, for the 2nd and 3rd sets of peaks, the presence of a peak on the higher angle side of the diffracted peaks that correspond to planes with Miller indices (220) and (310) at angles $\theta \approx 28.48^\circ$ and $\theta \approx 31.91^\circ$, was observed for all quantities other apart from when ~ 10 % moles of Br$_2$ added, as shown in figures 4.3 c and 4.3 d, respectively. Also, when ~ 20 % moles of Br$_2$ added, diffraction peaks that correspond to unreacted PbI$_2$ were noted as indicated with asterisks, in figure 4.3 a. It is assumed, when ~ 20 % moles of Br$_2$ are added, results in a depletion of the iodide content during the synthesis of doped CH$_3$NH$_3$PbI$_3$ micro-

\[\text{Figure 4.3: XRD patterns of CH$_3$NH$_3$PbI$_3$ micro-crystals synthesized using almost stoichiometric MC2 PbI$_2$ in reaction with equimolar plus an excess 10 % by weight of CH$_3$NH$_3$I, 14 % moles of CH(NH$_2$)$_2$I and controllable amount of Br$_2$ added. (a) for diffracted angle 2$\theta$ from 9° to 55°, (b) 1st set of peaks for diffracted angle 2$\theta$ from 11° to 16°, (c) 2nd set of peaks for diffracted angle 2$\theta$ from 27° to 30° and (d) 3rd set of peaks for diffracted angle 2$\theta$ from 30° to 33°. XRD peaks that correspond to crystallographic planes with Miller indices (200) and (110), referred to the perovskite with tetragonal crystal structure. Asterisks correspond to unreacted PbI$_2$. Normalization in all XRD patterns, was in respect to XRD peak that corresponds to crystallographic plane with Miller indices (110).} \]
crystals through formation of interhalogen compounds with general chemical formula $XY_n$, where $n \geq 1$, $Y$ are the bromide ions and $X$ are the less electronegative iodide ions. Consequently, the amount of dopant with respect to the size of the effective ionic radius of $A$ and $X$ ions substituted into the crystal structure of the $PbI_2$, is directly related to the specific number of moles used, resulting in a minimum of distortion of the crystal structure of the $CH_3NH_3PbI_3$. The synthesised micro-crystals were categorised as A, B, C and D type, with respect to the percentage of dopants used, providing an estimation of their chemical formula alongside with their molecular weight, as summarised in table 4.1. The calculation of the estimated molecular weight of each perovskite, was based on the summation of the atomic mass units for the estimated stoichiometry taking into account the ratio of elements present in each corresponding chemical formula.

<table>
<thead>
<tr>
<th>Type of micro-crystals</th>
<th>Percentage of materials used (based on $PbI_2$ moles)</th>
<th>Estimated chemical formula</th>
<th>Estimated molecular weight (g * mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$PbI_2$ + equimolar plus 10 % by weight of $CH_3NH_3$I + 40 % moles of $CH_3NH_3Br$</td>
<td>$CH_3NH_3PbI_{2.6}Br_{0.4}$</td>
<td>601.18</td>
</tr>
<tr>
<td>B</td>
<td>$PbI_2$ + equimolar plus 10 % by weight of $CH_3NH_3$I + 14 % moles of $CH(NH_2)_2$I</td>
<td>$(CH_3NH_3)_{0.86}(CH(NH_2)<em>2)</em>{0.14}PbI_3$</td>
<td>621.80</td>
</tr>
<tr>
<td>C</td>
<td>$PbI_2$ + equimolar plus 10 % by weight of $CH_3NH_3$I + 14 % moles of $CH(NH_2)_2$I + 10 % moles of $Br_2$</td>
<td>$(CH_3NH_3)<em>{0.86}(CH(NH_2)<em>2)</em>{0.14}PbI</em>{2.8}Br_{0.2}$</td>
<td>612.40</td>
</tr>
<tr>
<td>D</td>
<td>$PbI_2$ + equimolar plus 10 % by weight of $CH_3NH_3$I</td>
<td>$CH_3NH_3PbI_3$</td>
<td>619.98</td>
</tr>
</tbody>
</table>

Table 4.1: Type of doped $CH_3NH_3PbI_3$ micro-crystals synthesised at temperature 90 °C for 24 hours, using the almost stoichiometric mechanochemical MC2 $PbI_2$ in reaction with equimolar plus an excess 10 % by weight of $CH_3NH_3$I and (A) 40 % moles of $CH_3NH_3Br$, (B) 14 % moles of $CH(NH_2)_2$I, (C) 14 % moles of $CH(NH_2)_2$I and 10 % moles of $Br_2$ and (D) no other dopant. Also, estimated chemical formula and molecular weight, is provided for each type of doped $CH_3NH_3PbI_3$ micro-crystals.
4.2.2 Morphology of doped CH$_3$NH$_3$PbI$_3$ micro-crystals by SEM

Morphological characterisation of the controllably doped CH$_3$NH$_3$PbI$_3$ micro-crystals fabricated using an optimum amount of CH$_3$NH$_3$Br, CH(NH$_2$)$_2$I and Br$_2$ as dopants, was performed by SEM. Minor differences were observed among the doped CH$_3$NH$_3$PbI$_3$ micro-crystals fabricated using an optimum amount of dopants, as shown by SEM images in figures 4.4 a, 4.4 b and 4.4 c. However, undoped CH$_3$NH$_3$PbI$_3$ micro-crystals shown less sharp edges in average, as seen in figure 4.4 d, in comparison with all the doped CH$_3$NH$_3$PbI$_3$ micro-crystals. This may be related with the transition from tetragonal to cubic crystal structure, in respect to the substitution of methylammonium with formamidinium cations and iodide with bromide anions, in A and X sites, respectively. Also, SEM images confirm the regular shape of the almost perfect cubic crystal structure adopted by the doped CH$_3$NH$_3$PbI$_3$ micro-crystals, as function of the amounts of dopants used.
Figure 4.4: Scanning electron microscopy (SEM) images of doped CH$_3$NH$_3$PbI$_3$ micro-crystals synthesised at temperature 90 ºC for 24 hours, using the almost stoichiometric mechanochemical MC2 PbI$_2$ in reaction with equimolar plus an excess 10 % by weight of CH$_3$NH$_3$I and (a) 40 % moles of CH$_3$NH$_3$Br, (b) 14 % moles of CH(NH$_2$)$_2$I, (c) 14 % moles of CH(NH$_2$)$_2$I and 10 % moles of Br$_2$ and (d) no other dopant. Scale bars represent 5 µm.

4.2.3 Morphology of thin films made of undoped or doped CH$_3$NH$_3$PbI$_3$ micro-crystals by AFM

Morphological characterisation of the thin perovskite films formed after deposition on glass, using the controllably doped or the undoped CH$_3$NH$_3$PbI$_3$ micro-crystals, was performed by atomic force microscopy (AFM). All perovskite thin films were fabricated by re-dissolving doped or the undoped CH$_3$NH$_3$PbI$_3$ micro-crystals in Dry DMSO with
concentration 1.13M. The vacuum assisted method was used, as presented in chapter 2 (see experimental section). Formation of two-dimensional randomly orientated layered structures within individual grains, were observed regardless of the level of doping in micro-crystals used. These layered structures have also been noted in literature and confirmed by AFM, as shown in figures 4.5 a, 4.5 b, 4.5 c and 4.5 d. The measured roughness and thickness of all the thin films fabricated using doped or undoped CH$_3$NH$_3$PbI$_3$ micro-crystals, was less than 12 nm and 300 nm (± 10 nm), respectively, as measured by AFM. Also, the consistency of the values of thickness measured in all perovskite thin films (at four different points on each sample), indicates that the concentration of all perovskite solutions (1.13 M) using doped or the undoped CH$_3$NH$_3$PbI$_3$ micro-crystals, was very consistent and accurately calculated based on the corresponding estimated molecular weights.

![Image](image_url)
4.2.4 Vis-IR spectra of perovskite thin films made of undoped or doped CH$_3$NH$_3$PbI$_3$ micro-crystals

Optical characterisation of perovskite thin films deposited on glass, using the controllably doped or the undoped CH$_3$NH$_3$PbI$_3$ micro-crystals, was performed by visible-infrared (Vis-IR) spectroscopy, as shown in figure 4.6. Also, the calculated optical band gap (E$_{\text{obg}}$) values of each perovskite thin film varies as function of the dopant used, as determined by the Tauc plots and shown in figure 4.7. When 14 % moles of CH(NH$_2$)$_2$I incorporated into the crystal structure of CH$_3$NH$_3$PbI$_3$, the resulting E$_{\text{obg}}$ was ~1.49 eV, additionally when 10 % moles of Br$_2$ were introduced, the corresponding E$_{\text{obg}}$ was ~1.52 eV. These changes with respect to the E$_{\text{obg}}$ of the undoped CH$_3$NH$_3$PbI$_3$, which was determined to be ~1.51 eV, indicates that the bigger effective ionic radius of CH(NH$_2$)$_2$I expanded the crystal lattice leading to an E$_{\text{obg}}$ reduction, while the addition of Br$_2$ with smaller effective ionic radius contracted the crystal lattice, results in an increase in E$_{\text{obg}}$. Also, introduction of 40 % moles of Br$_2$ into the CH$_3$NH$_3$PbI$_3$, causes further contraction of crystal lattice, leading to an even...
higher value of the $E_{\text{obg}}$ ($\sim 1.54$ eV). In addition, thin films fabricated using the undoped CH$_3$NH$_3$PbI$_3$ micro-crystals, shown a weaker absorption of photons with energy $\sim 1.55$ eV in comparison with all thin films fabricated using the controllably doped CH$_3$NH$_3$PbI$_3$ micro-crystals, as shown in figure 4.7, which might be due to the different crystal structure adopted.

Figure 4.6: Visible-infrared (Vis-IR) absorption spectra of thin films fabricated by doped of undoped CH$_3$NH$_3$PbI$_3$ micro-crystals synthesised, using the almost stoichiometric mechanochemical MC2 PbI$_2$ in reaction with equimolar plus an excess 10 % by weight of CH$_3$NH$_3$I and 40 % moles of CH$_3$NH$_3$Br (red curve), 14 % moles of CH(NH$_2$)$_2$I (magenta curve), 14 % moles of CH(NH$_2$)$_2$I and 10 % moles of Br$_2$ (black curve) and no other dopant (green curve).
4.2.5 Implications of undoped or doped CH₃NH₃PbI₃ micro-crystals to perovskite solar cells

Perovskite solar cells consisting of sequence of stacking layers in the order: glass / ITO / SnO₂ / CH₃NH₃PbI₃ / Spiro-MeOTAD / Au which corresponds to n – i – p (regular) architecture were fabricated. The devices were tested, in order to determine whether the doping improves the device performances, with respect to the optimum amount of dopant ions in the perovskite structure. Preparation of solutions and related steps followed for the fabrication of PSCs, were exactly the same as presented in chapter 3 and experimental section (chapter 2). Also, the prepared solutions of doped / undoped CH₃NH₃PbI₃ micro-crystals were dissolved in dry DMSO. It was noted that they remained free of premature crystallisation inside the vials after filtration using a PTFE
filter with a pore size of 0.45 μm for more than 300 hours whilst stored at room temperature, as shown in figure 4.8. In addition, the HTL layer (spiro-MeOTAD) deposited was free of FK209 cobalt dopant agent. The photovoltaic parameters, Fill Factor (FF), short circuit current (Jsc), open circuit voltage ( Voc) and power conversion efficiency (PCE) of un-encapsulated PSCs devices were measured immediately after fabrication and after being kept for 120 hours and 240 hours in a plastic box covered with aluminium foil at ambient conditions. The results are illustrated graphically in figure 4.9. Measured data corresponds to the reverse scan (Voc → 0) with a scan step of 100 mV.

![Figure 4.8: Vials with dissolved doped or undoped CH3NH3PbI3 micro-crystals in dry DMSO with concentration 1.13 M after filtered and stored at room temperature for more than 300 hours. Doped or undoped CH3NH3PbI3 micro-crystals fabricated using, (A) 40 % moles of CH3NH3Br, (B) 14 % moles of CH(NH2)2I, (C) 14 % moles of CH(NH2)2I and 10 % moles of Br2 and (D) no other dopant. Scale bar, represents 20 mm.](image-url)
Figure 4.9: The Fill Factor (FF), short circuit current (J_sc), power conversion efficiency (PCE) and open circuit voltage (V_oc) of PSCs devices with structure glass / ITO / SnO_2 / CH_3NH_3PbI_3 / Spiro-MeOTAD / Au, as a function of time (fresh, after 120 hours or 240 hours) and the photoactive layer fabricated using doped or undoped CH_3NH_3PbI_3 micro-crystals, ((A) 40 % moles of CH_3NH_3Br, (B) 14 % moles of CH(NH_2)_2I, (C) 14 % moles of CH(NH_2)_2I and 10 % moles of Br_2 and (D) no other dopant).

The largest deviation of the average photovoltaic parameters (FF, V_oc, J_sc and PCE), was observed when the photoactive layer was fabricated with doped CH_3NH_3PbI_3 micro-crystals using 40 % moles of CH_3NH_3Br, as shown in figure 4.10. It was also noted that, when Br^- ions were introduced either by using CH_3NH_3Br or Br_2, the corresponding average values of FF, were initially increased after 120 hours, following a downward trend after 240 hours. While the V_oc values, were the highest in fresh PSCs, which may relate to the larger values of band gap, lower concentration of defects present in the synthesised micro-crystals and transition from tetragonal to cubic crystal structure. Whereas, absence of Br^- ions into the doped CH_3NH_3PbI_3 micro-crystals, results in an upward trend of the FF values even after 240 hours of
fabricated PSCs. Regardless of the type of perovskite micro-crystals used, the average values of J_sc in all devices shown a reduction after 120 hours, followed by an increase after 240 hours of storage. The similar trend to the J_sc, was noted for the average values of PCE. However, PCE values of PSCs devices fabricated using undoped CH_3NH_3PbI_3 micro-crystals, were constantly increased in respect to the time of their storage. Also, significant reduction of the V_oc average values as function of time, were observed in all PSCs made using doped CH_3NH_3PbI_3 micro-crystals, except of those made using undoped CH_3NH_3PbI_3 micro-crystals.

Figure 4.10: Average values (solid point) and corresponding deviations of the Fill Factor (FF), short circuit current (J_sc), power conversion efficiency (PCE) and open circuit voltage (V_oc) of PSCs devices with structure glass / ITO / SnO_2 / CH_3NH_3PbI_3 / Spiro - MeOTAD / Au, as a function of time (fresh, after 120 hours or 240 hours) and the photoactive layer fabricated using doped or undoped CH_3NH_3PbI_3 micro-crystals, ((A) 40 % moles of CH_3NH_3Br, (B) 14 % moles of CH(NH_2)_2I, (C) 14 % moles of CH(NH_2)_2I and 10 % moles of Br_2 and (D) no other dopant).
The current density-voltage of all PSCs devices that correspond to the forward scan (0 → V_{OC}) with a scan step of 100 mV, were further analysed and correlated with the time of storage and type of perovskite used. In all the following plots, black curves correspond to the average of current density-voltage curves and the coloured stripes represent the deviation between each initially recorded current density-voltage curve and the black curve. The characteristic green, red and cyan coloured stripes correspond to current density-voltage data of PSCs collected from fresh, after 120 hours and 240 hours, respectively, as shown in figure 4.11. While the characteristic orange coloured stripes correspond to current density-voltage data of fresh PSCs, collected at reverse scan (V_{OC} → 0) with a scan step of 100 mV. In all sets of black curves that express the average current density-voltage, green coloured stripes that represent the measurements of fresh PSCs, are above the red and cyan coloured stripes, after storage of the PSCs by 120- or 240-hours. Also, when Br⁻ ions were substituted into the CH₃NH₃PbI₃ micro-crystals, either by using CH₃NH₃Br or Br₂, result in a more enhanced shape (better FF) of the current density-voltage indicative of a p-n junction, as shown in figures 4.11 a and 4.11 c. Consequently, the degree of hysteresis observed at the current density-voltage curves between forward and reverse scans, might directly related with the crystal lattice of perovskite during its crystallisation process, in respect to the crystal lattice or surface energy of substrate used. Specifically, the crystal lattice mismatch or surface energy at the interface between perovskite / SnO₂, may be responsible hosting only a maximum number of ions during the crystallisation of perovskite via halogen-oxygen covalent bonds formed. The introduction of ultra violet (UV) ozone treatment of the SnO₂ increases the concentration of oxygen via formation of hydroxyl groups or stannate tin (Sn(OH)₄), leading to an enhanced number of those covalent bonds to be formed and reducing the hysteresis within the current density-voltage curves between forward and reverse scans. However, we suggest that a controllably in stoichiometry deposited thin layer (< 5 nm) of perovskite metal - oxide type on TCO, might provide the necessary number of halogen-oxygen bonds, resulting in more stable PSCs. This approach is analogous with the growth of III-V doped semiconducting materials with optimum optoelectronic properties by molecular beam epitaxy (MBE), for controllable transition between the thin films with different crystal lattices.
Figure 4.11: Characteristic current density-voltage curves in forward ($0 \rightarrow V_{OC}$) and reverse ($V_{OC} \rightarrow 0$) scans of PSC devices with structure glass / ITO / SnO$_2$ / CH$_3$NH$_3$PbI$_3$ / Spiro-MeOTAD / Au, as a function of time and the photoactive layer fabricated using doped or undoped CH$_3$NH$_3$PbI$_3$ micro-crystals, (a) 40 \% moles of CH$_3$NH$_3$Br, (b) 14 \% moles of CH(NH$_2$)$_2$I, (c) 14 \% moles of CH(NH$_2$)$_2$I and 10 \% moles of Br$_2$ and (d) no other dopant. Black curves correspond to the average of current density-voltage curves and coloured stripes to their deviation from the average black curve. Green, red and cyan coloured stripes, indicate current density-voltage data collected from fresh, after 120 hours and 240 hours, in forward ($0 \rightarrow V_{OC}$) scans. Whereas orange coloured stripes, indicate current density-voltage data collected from fresh, in reverse ($V_{OC} \rightarrow 0$) scans.
4.3 Conclusion

In conclusion, synthesis of controllably doped CH$_3$NH$_3$PbI$_3$ micro-crystals with variable amount of dopants of either CH$_3$NH$_3$Br or CH(NH$_2$)$_2$I or CH(NH$_2$)$_2$I and Br$_2$, was successfully achieved without dissolving the PbI$_2$ used in highly toxic solvents. The optimum amount of ions selectively intercalated into the crystal structure of CH$_3$NH$_3$PbI$_3$, was defined by the transition from tetragonal to cubic crystal structure, as determined by the XRD spectra and SEM images. Also, crystal structure transition in perovskite caused by the substitution of ions with different effective ionic radius, was correlated with optical band gap values, as determined by Vis-IR spectra. However, more than one transition in the crystal structure, might exist with respect to the amount and effective ionic radius of ions used. Perovskite thin films manufactured by re-dissolving the doped or undoped CH$_3$NH$_3$PbI$_3$ micro-crystals only in DMSO solvent which is less-toxic than the widely used dimethyl formamide (DMF) solvent. In combination with a single step of fabrication, using a vacuum assisted method, free of any complicated step that promotes the crystallisation of perovskite using the method of antisolvent. Morphological characterisation of thin films, revealed the formation of two-dimensional layered structures within the perovskite grains, regardless of the ratio between the cations and anions used, as determined by AFM images. The PSC devices fabricated, showed a reduction in the average PCE from ~ 14 (±1.5) % to ~ 13.7 (±0.5) %, after storage under ambient conditions for 240 hours, regardless of the ratio between the cations and anions present into the doped or undoped CH$_3$NH$_3$PbI$_3$ micro-crystals used. Additionally, PSCs devices fabricated using photoactive layers doped with bromide anions, shown less hysteresis at the current density-voltage curves at forward scans.

4.4 References


Chapter 5

Conclusions and future work

5.1 Introduction

Since the end of the previous decade, when the scientific community became aware of their remarkable and versatile optoelectronic properties, mixed organic - inorganic halide perovskite compositions with general chemical formula ABX₃, have emerged as a new class of semiconductors. Noticeable progress has been made worldwide by numerous researchers, implementing them in devices, such as photovoltaics, light emitting diodes (LEDs), photodetectors, batteries and even in the field of spintronics.¹⁻⁵ Rapid progress in the field of perovskite solar cells (PSCs) development, originates from the low cost of the materials used, variability in the optoelectronic properties as a function of the ratio between the mixed organic-inorganic halide precursors and their simplicity of fabrication. Also, astonishing values (~ 24 %) for the power conversion efficiency (PCE) in PSCs, based on a single photoactive layer of perovskite have been achieved. This performance, competes with the market dominating silicon based solar cells with PCE ~ 26.6 %. The current state of the art of devices combine together silicon and perovskite materials to result in tandem heterojunction photovoltaic devices, which reach a PCE of 28 %, as shown in the NREL (National Renewable Energy Laboratory) chart of the highest PCE values per type of photovoltaic (see figure 1.8 in chapter 1). However, long term stability and durability, remain key challenges for PSC commercialization. These parameters will be influenced by the purity and stoichiometry of the organic-inorganic halide precursors used in the fabrication of perovskites.
5.2 Conclusions

In this thesis, the importance of stoichiometry and polytypism in lead iodide (PbI$_2$) used in the PSCs fabrication process, was studied as presented in chapter 3. Successful synthesis of PbI$_2$ was achieved by employing two different methods of synthesis and their properties were compared with two commercially available materials. The two processes used were the solvothermal in which there was presence of water and a mechanochemical approach using planetary ball milling which was free of water during the synthesis of PbI$_2$. The solvothermal synthesis results in over-stoichiometric PbI$_2$, with a lead to iodide ratio be 1:~2.05 (±0.05), as determined by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS). Also, a high percentage of oxygen content (~7.2 %) possibly attributed to autoionization of water molecules caused by strong Coulomb interactions between the ions (Pb$^{2+}$ and I$^-$) and water molecules was detected by energy dispersive spectroscopy (EDS) predominantly in the needle shaped crystals present. That increased oxygen content was guide us to the mechanochemical approach which was free of water. Mechanochemical synthesis allowed regulation of both the stoichiometry and the number of polytypic phases present in the resulting PbI$_2$, as shown by X-ray diffraction (XRD). By varying the mechanochemical parameters (revolution per minute and time duration) of the synthesis, we found that at optimum conditions of 400 rpm and 1 hour, results in PbI$_2$ with lead to iodide ratio be from 1:2, as determined by XPS and RBS analysis, respectively. It should also be noted, that the mechanochemical method, is a low-cost, water free and energy efficient (~ 31.3 watts per hour per gram) process, producing moderate to large quantities of PbI$_2$ (≥ 40 grams per run and yield ~ 96 ±0.5 %). In contrast, the two commercial PbI$_2$ powders were found to be sub- or over-stoichiometric with a single or more than one polytypic phase materials. The ratio between the lead to iodide atoms was 1: ~ 1.8 (±0.1) for the Sigma Aldrich with purity 99.999 % and 1: ~ 2.15 (±0.15) for the Tokyo Chemical Industries with purity 99.99 %, as determined by XPS, RBS and XRD analysis, respectively. Also, the stoichiometric ratio between the lead and iodide atoms present for the mechanochemical was found to be 1: ~ 1.96 and the commercial from Sigma Aldrich to be 1: ~ 1.7 as determined and corrected by controllable synthesis of CH$_3$NH$_3$PbI$_3$ micro-crystals, as shown by XRD characterisation. This discrepancy at stoichiometric ratios between the lead and
iodide atoms in PbI₂ samples as determined by different characterization techniques might be related to a formatted gradient of iodide atoms between the surface and bulk (inner volume) directly correlated with the polytypic nature of PbI₂. PSC devices fabricated with CH₃NH₃PbI₃ thin films as the photoactive layers, manufactured using sub-stoichiometric PbI₂, showed a reduction in the average power conversion efficiency (PCE) from ~15.5 % to ~4.6 % due to the presence of unreacted PbI₂, as further confirmed by Vis-IR spectroscopy. A comprehensive analysis was presented regarding the formation of unreacted PbI₂ in respect to the initial stoichiometry of the PbI₂ used for the formation of CH₃NH₃PbI₃. However, when excess iodide added to the sub-stoichiometric PbI₂ via CH₃NH₃I during the fabrication of CH₃NH₃PbI₃ microcrystals, the average performance of PSCs was high (~15.5 %). Also, CH₃NH₃PbI₃ thin films were manufactured using only dimethyl sulfoxide (DMSO) which is a less-toxic solvent in comparison with the widely used dimethyl formamide (DMF) solvent. Deposition of perovskite thin films combined with a single step of a vacuum assisted method, promoted the formation of two-dimensional CH₃NH₃PbI₃ layered structures within individual grains, regardless of the stoichiometry and polytypic phases present in the PbI₂ used, as shown in AFM and SEM images. We believe, that an ideal stoichiometry of materials used in the synthesis of the perovskite thin films, alongside with a simple and repeatable deposition process for the fabrication of PSC devices, might provide enhanced stability and PCE values.

The stability of PSCs fabricated with optimum stoichiometry between different ions present was assessed, as presented in chapter 4. Synthesis of controllably doped or undoped CH₃NH₃PbI₃ micro-crystals with various amounts of dopants of either methylammonium bromide (CH₃NH₃Br) or formamidinium iodide (CH(NH₂)₂I) or CH(NH₂)₂I and bromide (Br₂), was achieved. An optimum amount of dopants defined by the transition from tetragonal to cubic crystal structure based on the three major peaks with the strongest diffraction, as determined by XRD spectra. An optimum amount ~40 % moles of Br⁻ ions substituted in the crystal structure of CH₃NH₃PbI₃ was found. Whereas, the optimum combined amount was found to be ~14 % moles of CH(NH₂)₂⁺ and ~20 % moles of Br⁻ ions substituted into the crystal structure of CH₃NH₃PbI₃. Also, optical band gap values of perovskite thin films fabricated using the controllably doped CH₃NH₃PbI₃ micro-crystals, shown fluctuation with respect to CH₃NH₃PbI₃. That was attributed to expansion or contraction in the crystal lattice of
perovskites, as function of the effective ionic radius of dopant ions used and confirmed by Vis-IR spectroscopy. PSC devices manufactured by re-dissolving the doped or undoped CH$_3$NH$_3$PbI$_3$ micro-crystals only in DMSO and crystalizing again as a thin film with the single step vacuum assisted method, results in the formation of two-dimensional perovskite layered structures within individual grains, regardless of the ratio between the cations and anions used, as determined by AFM / SEM images. Also, un-encapsulated PSC devices with stacking sequence of glass / ITO / SnO$_2$ / CH$_3$NH$_3$PbI$_3$ / Spiro-MeOTAD / Au showed a small reduction in the average PCE from ~ 14 (±1.5) % to ~ 13.7 (±0.5) % after storage in dark and under ambient conditions for 240 hours. Additionally, PSC devices fabricated using photoactive layers doped with Br anions, shown less hysteresis in the current density-voltage curves between the forward (0 → V$_{OC}$) and reverse (V$_{OC}$ → 0) scans. We believe, this might originated from the number of halogen-oxygen covalent bonds formed at the interface between the perovskite thin film during the crystallisation and the untreated (without the ultra violet light ozone) electron transporting layer of tin oxide (SnO$_2$) used.

5.3 Future work

An extension to the work undertaken in chapter 3, would be the investigation of PbI$_2$ synthesis for identical stoichiometry by using a mixer mill MM 400 (Retsch), which is an entirely new type of mechanochemical process for powder homogenization, with typically grinding time from seconds to minutes. This process might require less time than the use of planetary ball milling, whilst maintaining a stoichiometrically accurate ratio in a range of chalcogenide compounds, such as cadmium iodide (CdI$_2$), lead chloride (PbCl$_2$), lead bromide (PbBr$_2$) etc., free of oxygen-halogen compounds. Also, PSCs devices manufactured by dissolving the organic-inorganic precursors or perovskite micro - crystals only in DMSO, which is a less-toxic solvent and combined with the single step vacuum assisted method, free of any antisolvent rinsing step, is likely to be an attractive deposition process for roll-to-roll or tandem (heterojunction of silicon / perovskite) development in the field of PSCs.

An extension to the work undertaken in chapter 4, would be the investigation of controllable doping of formamidinium lead triiodide CH(NH$_2$)$_2$PbI$_3$ micro-crystals with
caesium iodide (CsI) and Br$_2$, in order the optimum amount of Cs$^+$ and Br$^-$ ions intercalated into the crystal structure to be determined by XRD spectra. Also, since the formation of two-dimensional perovskite layered structures were observed, regardless of the ratio between the cations and anions used. Progressive annealing of perovskite thin films directly after the step of vacuum assisted method, in a chamber with pressure (P): 1 bar < P < 50 bar, might accelerate the formation of the two-dimensional layered structures in a preferable orientation, resulting in perovskite thin films with larger grains and reduced number of grain boundaries. In principle, this process is similar to gas (nitrogen) quenching which, resulting in densely packed grains in perovskite thin films.  

During the electrical characterisation of un-encapsulated PSCs fabricated with photoactive layers doped with bromide, less hysteretic effect was observed between the current density-voltage curves recorded at forward and reverse scans. Considering that ultra violet ozone treatment leads to elimination of hysteresis in PSCs by hydroxyl groups formed on the electron transporting layer (ETL) on which the crystallisation of perovskite thin film occurs. We suggest that deposition of a metal-oxide perovskite layer between the ETL and the photoactive layer of perovskite, might provide an adequate number of oxygen atoms and therefore more halogen-oxygen covalent bonds to be formed. That metal-oxide perovskite layer, could provide a crystal lattice transition between the ETL and the photoactive layer, likely leading to enhanced optoelectronic properties and stability in PSCs.

Lastly, there is an increasing number of technological devices, such as mobile phones, computers, cars, space equipment, satellites etc., electrified by batteries and thermoelectric modules. Since, batteries and thermoelectric modules can now be fabricated based on perovskites and have shown enormous values of current capacity (200 mA * h * g$^{-1}$) and Seebeck coefficient (~ 1700 $\mu$V * K$^{-1}$ at temperature of 351 K).  

It is highly probable that batteries and thermoelectric modules fabricated using controllable doped perovskites micro-crystals, will gain significant attention in the near future.

5.4 References