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Stability Evaluation and Degradation Pathways of Metal Halide Perovskite Thin Films

Department of Mechanical and Materials Engineering

Bachelor's thesis

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The growing demand for sustainable energy and the finite nature of fossil fuels have increased the interest in alternative photovoltaic technologies. Metal halide perovskites have emerged as promising materials due to their high power conversion efficiency, low-cost fabrication, and excellent optoelectronic properties. However, their limited long-term durability under environmental conditions remains a significant barrier to commercialisation, making the understanding of degradation mechanisms crucial.

This bachelor's thesis is a literature review focusing on the stability of metal halide perovskite thin films and the key degradation pathways that affect their performance. The thesis focuses on commonly studied materials, such as methylammonium lead halides, and examines the effects of major extrinsic factors, including moisture, heat, light, and oxygen, together with their combined effects. In addition, intrinsic factors, such as ion migration and grain boundaries, are briefly discussed in relation to material instability.

The thesis also reviews the characterisation and evaluation methods commonly used to analyse the ageing of perovskite thin films, including structural, morphological, and optoelectronic techniques. Overall, this work summarises current knowledge on stability issues in perovskite thin films and emphasises the importance of ongoing research to improve the durability and practical applicability of perovskite solar cells.

Keywords: Perovskite material, thin films, stability, evaluation methods.

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Kestävän energian kasvava kysyntä ja fossiilisten polttoaineiden rajallisuus ovat lisänneet kiinnostusta vaihtoehtoisiin aurinkosähköteknologioihin. Metallihalidiperovskiitit ovat osoittautuneet lupaaviksi materiaaleiksi niiden korkean energianmuuntotehokkuuden, alhaisten valmistuskustannusten ja erinomaisen optoelektronisten ominaisuuksien ansiosta. Niiden rajoitettu kestävyys ympäristöolosuhteissa on kuitenkin edelleen merkittävä este kaupallistamiselle, minkä vuoksi hajoamisprosessien ymmärtäminen on erityisen tärkeää.

Tämä kandidaatin tutkielma on kirjallisuuskatsaus, joka keskittyy metallihalidiperovskiittiohutkalvojen vakauteen ja suorituskykyyn vaikuttaviin keskeisiin hajoamisreitteihin. Tutkielma keskittyy yleisesti tutkittuihin materiaaleihin, kuten metyyliammonium-lyijyhalideihin, ja tarkastelee tärkeimpien ulkoisten tekijöiden, kuten kosteuden, lämmön, valon ja hapen vaikutuksia sekä niiden yhteisvaikutusta. Lisäksi materiaalin epävakauteen liittyviä sisäisiä tekijöitä, kuten ionien siirtymistä ja raerajoja käsitellään lyhyesti.

Tutkielmassa käsitellään myös yleisesti käytettyjä karakterisointi- ja arviointimenetelmiä perovskiittiohutkalvojen ikääntymisen analysoimiseksi. Näihin sisältyvät muun muassa rakenteelliset, morfologiset ja optoelektroniset tekniikat. Tämä työ tiivistää nykyistä tietämystä perovskiittiohutkalvojen vakauteen liittyvistä ongelmista sekä korostaa jatkuvan tutkimuksen merkitystä perovskiittiaurinkokennojen kestävyyden ja käyttökelpoisuuden parantamiseksi.

Avainsanat: Perovskiitti, ohutkalvo, vakaus, arviointimenetelmät.

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1 Introduction

Global energy consumption continues to increase, and the scarcity of fossil fuels requires us to search for more sustainable options to match the energy needs of the ever-growing population. A promising solution is photovoltaic (PV) technology, which can convert sunlight into electricity, through devices known as solar cells [1].

In the current situation, first-generation solar cells dominate the market [2]. Silicon-based solar cells have established manufacturing processes, relatively abundant materials, and proven efficiency and stability [3]. Of all the commercial solar cells on the market, over 80% are produced from silicon [4]. Yet, scientists are currently looking for alternative solutions that can be even more cost-effective and more environmentally friendly. So far, there are many different materials being studied, and perovskite solar cells (PSCs) are one of them [2]. PSCs have gained significant interest among scientists because of their increasing power conversion efficiencies (PCEs) of up to 27.02% that can match the currently used photovoltaic technologies [5]. Latest research shows even higher PCE of 27.3%, which can be seen from the NLR.gov “Best Research-Cell Efficiencies” chart [6].

The high photovoltaic performance of PSCs arises from their intrinsic properties like superior carrier mobility, tuneable bandgap, high absorption coefficient, and ambipolar carrier transport [2]. PSCs also have the potential of being a viable option for being an economical source of energy, considering the current issues with climate change [7]. In the device structure, the perovskite material functions as an absorber layer or film between electron transport layer (ETL) and hole transport layer (HTL). When the perovskite material absorbs sunlight, it generates electrons and holes into different carrier-transporting materials (n-type and p-type) to generate free charge carriers. Then the generated electrons reach the cathode after traveling through ETL and an external circuit, while the HTL restores the oxidised perovskite and helps it to return to the ground state. Thus, the holes are collected at the anode, resulting in the generation of photocurrent through the external circuit [2].

1.1 Perovskite materials and thin films

Organic-inorganic hybrid perovskite (OIHP) with an ABX_3 (Figure 1) structure is the most promising candidate so far for achieving the required cost-effectiveness and

efficiency as an absorption layer [2]. In the ABX_3 chemical structure, A refers to a positive monovalent cation like cesium (Cs^+), formamidinium (FA^+, $CH(NH_2)_2^+$), or methylammonium (MA^+, $CH_3NH_3^+$); B is a positively charged divalent metal like lead (Pb^{2+}) or tin (Sn^{2+}); and X stands for negatively charged halide ions like iodine (I^-), chlorine (Cl^-) or bromide (Br^-) [2,7]. Among all different perovskite materials, methylammonium lead halide structures ($MAPbX_3$) have been one of the most common absorption layers in photovoltaic applications [8]. Recent studies also prefer composition engineering, where for example different cation groups (e.g., $FA_{1-x}MA_xPbI_3$) are used to maximise stability and efficiency of the created films [5]. The major challenges associated with these types of perovskite include the presence of toxic lead and their relatively low stability, which acts as a barrier for commercialisation [2].

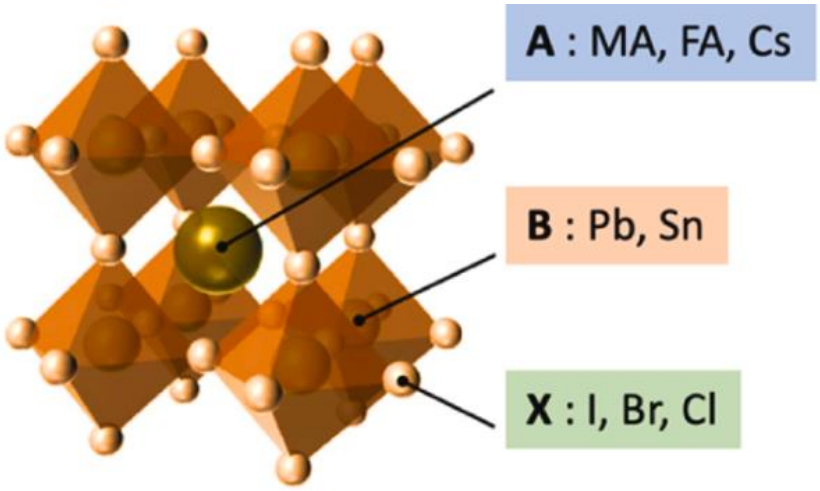

Figure 1. Schematic of perovskite structure with a chemical formula of ABX_3. (Modified from Widianto et al. [9]. Copyright 2025 Widianto et al., published by Journal of Science: Advanced Materials and Devices.)

OIHPs were also studied for light-emitting diode and transistor applications in the 1990s by Mitzi and colleagues, since they have many unique electrical and optical properties for example: large Bohr radius, high carrier diffusion velocity and diffusion length, low exciton binding energy, high dielectric constant, and finally very large light absorbing capacity [2]. On-chip coherent light sources could also be one of the applications for OIHPs, thanks to their high photoluminescence [10].

1.2 Stability challenges in perovskite materials

PSCs have gained significant attention in recent years for their high PCE, low-cost fabrication, and relatively easy manufacturing [1]. However, significant challenges remain regarding PSC instability and ageing, which mainly originates from the intrinsic instability of perovskite materials [7]. The most common pathways and mechanisms for PSC degradation can be divided into two main categories: intrinsic factors and extrinsic factors. The intrinsic factors are related to material microstructural and chemical instability phenomena, while the extrinsic ones involve ambient factors such as humidity, temperature, and other environmental conditions [1]. Addressing degradation mechanisms in perovskite materials is one of the most important factors for improving the long-term stability of PSCs and eventually commercialisation [7].

1.3 Aim and scope of this literature review

This thesis is a literature review that focuses on the dominant environmental factors for ageing on the most common perovskite materials, such as $MAPbI_3$. These environmental factors include humidity, thermal stress, light, and oxygen. Since PSCs' typical usage will happen under the influence of multiple stress sources, these kinds of scenarios are addressed as well. This is then followed by degradation characterisation techniques, which are discussed to give insight into how these types of unique materials can be evaluated using modern equipment.

2 Stability of perovskite thin films

Perovskites are soft semiconductor materials in which the chemical elements form many different types of bonds. These can be strong ionic bonds, weaker hydrogen bonds, and van der Waals forces [11]. The inorganic components of the structure also form an extensive network of directional covalent bonds, which can explain the precise crystal structure of the layered films [12].

The long-term use of perovskite-based devices requires the ability to withstand the effects of extrinsic factors, including high humidity and temperature, oxygen, and light, along with the problems associated with intrinsic factors like grain boundaries, hysteresis, and nonradiative carrier recombination [5]. According to the International Electrotechnical Commission (IEC), especially the IEC 61215 qualification test requires the applied PV technologies to retain a minimum of 95% of initial PCE after 1000 h of being subjected to a temperature of 85 °C at 85% relative humidity (RH), as well as other methods like thermal cycling and humidity / freeze tests to ensure a lifetime of 25 years [13].

The OIHP materials combine the beneficial effects of organic and inorganic cage structures. In this type of structure, the metal cation (B) defines the electronic properties by the creation of metal-halide hybridised orbitals. The organic cation (A) defines the structure and dimensions as well as directly affects the material's stability and optoelectronic properties [12]. For example, the A-site containing organic cations such as FA or MA is usually prone to thermal degradation, leaving PbX_2 as a breakdown product [13].

One of the main degradation methods for $MAPbI_3$ films is the formation of PbI_2, which can be driven by thermal annealing [14] or other ambient conditions [11]. This form of decomposition can be observed visually from the colour of the films. Normally, the $MAPbI_3$ films are black, but due to the formation of PbI_2 in the films, they turn yellow [14].

This chapter provides an overview of the various factors affecting the degradation of perovskite thin films, including four of the major extrinsic factors shown in Figure 2, as well as some insight into ion migration and crystal defects. The chapter presents a

broad analysis of mechanisms underlying the instability of perovskite films by reviewing existing research data.

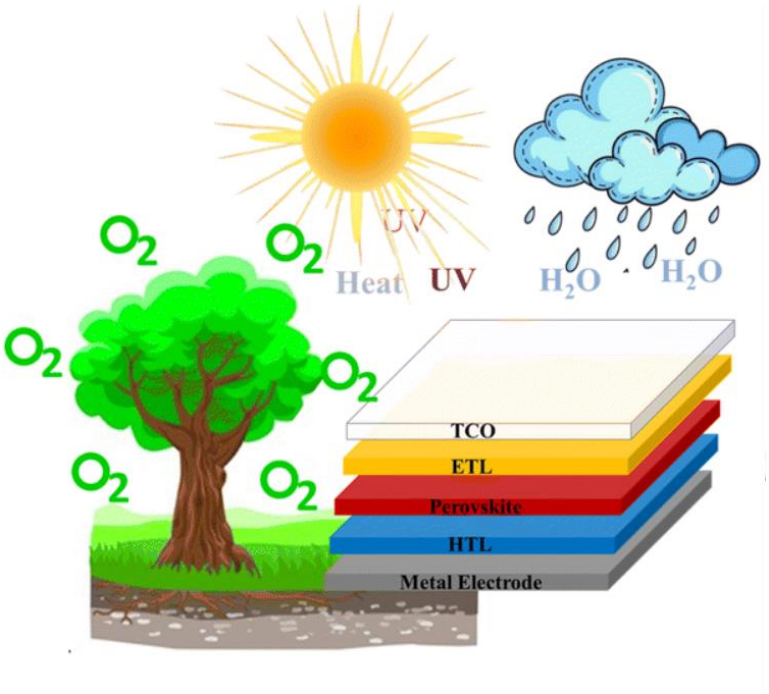

Figure 2. Extrinsic factors affecting PSC stability. (Modified from Miah et al. [11]. Copyright 2025 Miah et al., published by The Royal Society of Chemistry; RSC Publishing; Cold Spring Harbor Laboratory Press.)

2.1 Moisture / relative humidity

Moisture is a major challenge considering the stability of OIHPs [7]. Due to the perovskite materials' solubility in protic polar solvents such as water, they degrade readily in humid environments. The main mechanism for degradation comes from the interaction of water molecules with perovskite materials' hydrogen bonds, which are typically between the organic cation and the inorganic metal-halide octahedral framework. This interaction causes the hydrogen bonds to break and form new hydrogen bonds and hydrated compounds [15]. This hydrophilic nature originates from the amine-salt like methylammonium (MA^+) in the commonly used perovskite structures such as $MAPbI_{3-x}Cl_x$ or $MAPbI_3$. The degradation in these materials occurs when MA decomposes, releasing volatile species such as methylamine and hydrogen iodide, leaving behind lead iodide (PbI_2) [7]. The irreversible hydrolysis reaction of $MAPbI_3$ can be seen from the chemical equations 1 through 4 [7,16]:

$$CH_3NH_3PbI_3(s) \rightarrow PbI_2(s) + CH_3NH_3I(aq) \quad (1)$$

$$CH_3NH_3I(aq) \rightarrow HI(aq) + CH_3NH_2(aq) \quad (2)$$

$$4\,HI(aq) + O_2(g) \rightarrow 2\,I_2(s) + 2\,H_2O(l) \quad (3)$$

$$2\,HI(aq) \rightarrow H_2(g) + I_2(s) \quad (4)$$

It is studied that the degradation process of $MAPbI_3$ occurs in 4 different stages, which are passivation of the surface, addition of free electrons, interfacial hydration, and finally mass hydration [16]. In the first stage, moisture is able to form hydrogen bonds rapidly with uncoordinated iodine ions in the molecule's surface, which suppresses nonradiative surface recombination [17]. In the second stage as water concentration increases, a continuous network consisting of water molecules is created, which fully covers the surface of the perovskite. The formed layer can work as a barrier to prevent water molecules from entering the perovskite. High-frequency water vibrations also enable the nonadiabatic coupling to grow in $MAPbI_3$ and shorten the excited state lifetime [18].

The latter stages are the ones with the most detrimental effects on the perovskite structure regarding performance, if the reactions with water continue all the way [16,19]. In the third stage, the water molecules get inside the perovskite structure through its crystalline surface, and hydroxide substitution on the halide lattice can be seen. After this, the MA^+ and $iodine^-$ ions escape from the lattice structure [19]. Then the surface layer of the Pb-I framework dissolves, which most likely then interacts with the organic species of the molecule. Finally, in the fourth stage, the excess water destroys the perovskite due to the hydration-decomposition process. This is possible because of the high chemical potential of water, which speeds up the perovskite transition to different monohydrated phases with a broader surface state band gaps [16].

Other environmental factors, such as oxygen exposure or UV light, can also accelerate the degradation by reducing the strength of the $CH_3NH_3^+$ hydrogen bonds. This causes a dramatic reduction in cell efficiency [16]. A study conducted by Chakraborty et al. [20] investigated the effects of environmental factors on the performance and long-term stability of PSCs using $MAPbI_2Cl$. In the study various, environmental conditions were tested to see the irreversible degradation caused by moisture, UV light, and temperature. During testing, RH was controlled to be between

30-38% and at high humidity of over 50%. These tests showed clear marks that elevated humidity levels in a similar environment increased the degradation speed of PSCs. PSCs in a lower RH lasted for around 28 hours, while the ones tested in high humidity only stood operational for around 14 hours [20]. Yet there are some studies that indicate that water is essential to a certain point to promote the growth of perovskite crystals and increase the performance of PSCs in other ways as well [16].

2.2 Thermal stress / heat

Heat is one of the major environmental factors associated with extrinsic degradation for PSCs, and especially for the most common perovskite materials, such as $MAPbI_3$ [21]. The instability of PSCs is mostly caused by decomposition of the crystal structure. In the case of ABX_3 -structured OIHPs, the A-site is typically prone to thermal decomposition, affecting the formation of PbX_2 [13]. $MAPbI_3$ is known to go through a phase transition at relatively low temperatures of 54-57 °C, in which the crystal structure changes from tetragonal to cubic phase. This happens due to its low formation energy and weak bonds in the original structure [21].

Yang et al. [14] studied the thermal instability of $MAPbI_3$ and observed the increasing formation of PbI_2 by elevated temperatures from 160 – 200 °C while studying grain size related thermal stability and performance in $MAPbI_3$ films. They explained the process via the following chemical equation [14]:

$$CH_3NH_3PbI_3(s) \leftrightarrow PbI_2(s) + CH_3NH_3I(aq). \quad (5)$$

Here we can see that the chemical equation for degradation shows the same reaction products as the one with humidity or equation 1, demonstrating the primary pathway for degradation in $MAPbI_3$. Tenuta et al. [22] researched the thermodynamic origin of instability in OIHPs and linked the thermodynamic calculations to match the previous equation 5 in the presence of water [22].

Recently, Yang et al. [13] showed a more detailed analysis of degradation in the formed salts used in perovskites containing organic cations such as MA^+ in a feature article published in 2025. In the article, they explained the thermal decomposition pathways via the following chemical equations:

$$CH_3NH_3X(s) \leftrightarrow CH_3NH_2(g) + HX(g), \quad (6)$$

$$CH_3NH_3X(s) \rightarrow NH_3(g) + CH_3X(g). \quad (7)$$

The first degradation method shown in equation 6 explains the deprotonation of the MA halide molecule, which can happen at temperatures ranging from 50-130 °C. The second method shows the demethylation reaction, which happens at much higher temperatures ranging from 300-420 °C. Due to the interatomic forces of different bonds in the structure, the deprotonation is more favourable, since it requires breaking the N-H hydrogen bond rather than the strong covalent bond of C-N. The deprotonation reaction can also be more reversible and have a longer lifetime due to a weakly stabilised intermediate state [13].

Annealing is commonly used and important for crystallisation of the perovskite phase in a solution-based fabrication of perovskite films. Considering the risk of damaging the perovskite itself through thermal processes [14], the temperature control is crucial for the formation of controlled sized perovskite crystals as well as managing other qualities of the films[23,24]. Yang et al. [14] have shown that thermal stability is mainly controlled by grain boundaries in polycrystalline hybrid perovskite thin films (e.g., $MAPbI_3$). Their study showed that increasing the grain size and having fewer grain boundaries increases the thermal stability of the film. The improved thermal stability is explained through different amounts of energy required for a reaction to happen within the grains and at grain boundaries. The activation energy for a reaction to happen is lower at grain boundaries because of dangling bonds, which have a low bond energy and higher surface energy. This makes the degradation happen more easily at those points of the lattice, which ultimately leads to a weaker structure [14].

2.3 Effects of Light

Light-induced degradation remains a major challenge with PSCs' stability, and a practical solution for mitigating this issue is still under development [25]. Illuminated perovskite materials tend to break down due to degradation of materials, despite being highly efficient light collectors for producing electron-hole charge carriers [21]. It has been found that high-energy UV light can cause the decomposition of the N-H bond in MA by inducing excited electrons into N-H antibonding orbitals, creating CH_3NH_2 and H_2 in the perovskite lattice [26]. UV light can also provide the chemical

potential that makes the iodide ions oxidise to I_2, which then tends to diffuse throughout the perovskite layer, causing it to degrade [25].

Another route for the degradation to happen in ambient conditions is via the generation of hydrogen iodide (HI), which comes from the MA cation [21]. The combination of light and dry air causes the perovskite films to deteriorate rapidly. Photoinduced electrons on the perovskite react with oxygen molecules to form a superoxide. This superoxide then reacts further with the MA cation [7]. Oxygen can also react with perovskite on the interface of titanium dioxide (TiO_2), which is one of the common ETL materials used in PSCs [27]. Further phenomena regarding oxidation reactions are discussed in Chapter 2.4. The currently known pathways for degradation to happen in perovskites regarding light effects can include catalytic photoinduced degradation in the presence of oxygen and light, and light-induced ion migration [28].

Light-induced degradation also happens more easily at elevated temperatures in complex lead halides and is inevitable under realistic operational conditions. Akbulatov et al. [29] studied the interplay between light and heat in $MAPbI_3$ and PbI_2 materials at temperatures of 30 °C, 45 °C, and 55 °C. Their studies showed clear marks that degradation happens both more rapidly and more severely with higher temperatures in $MAPbI_3$ thin films. Furthermore, the formation of metallic lead was found to be suppressed at lower temperatures (30 °C), which indicates temperature control to be a possible solution for longer-lasting thin films [29].

To be more specific on the effect of light on perovskite materials, many studies have used vacuum conditions to exclude other forms of deterioration during testing. For example, Tang et al. [13] used light and dark vacuum conditions to discover the degradation in $MAPbI_3$. In situ X-ray diffraction showed the degradation of $MAPbI_3$ with the corresponding increase in PbI_2 under illumination compared to dark conditions. The formation of metallic lead was only found after illumination, which indicates decomposition induced by light [13]. In addition, light energy greater than 2.5 eV can make PbI_2 decompose further to I_2, which then reacts with other breakdown products and eventually leads to the formation of volatile species such as CH_3NH_2 and H_2 that leave the perovskite material. The irreversible reactions can be seen from the following equations [30]:

$$PbI_2(s) \xrightarrow{2.5\ eV} Pb^0(s) + I_2(s), \quad (8)$$

$$I_2(s) \xrightarrow{hv} 2\ I^{\bullet}(s), \quad (9)$$

$$2\ I^-(s) + 2\ I^{\bullet}(s) \xrightarrow{hv} 2\ I_2^{\bullet -}(s), \quad (10)$$

$$2\ CH_3NH_3^+(s) + 2\ I_2^{\bullet -}(s) \xrightarrow{hv} 2\ CH_3NH_2(g) + 2\ I_2(s) + H_2(g). \quad (11)$$

Wang et al. [28] discussed in their review article about another study made by Li et al., which researched white light effects on $MAPbI_3$ under ultra-high vacuum. Their research also confirms the permanent degradation of PSCs even in vacuum conditions. Their study also indicates the presence of CH_3I (s) as a reaction product, which indicates further degradation of the methylammonium. One of the more interesting phenomena they observed was the formation of a protective layer on the surface of the perovskite film, which can block further decomposition of the material. This can be explained by the absorption of the reaction products by the perovskite itself, although it can have its drawbacks on performance [28].

OIHP materials differ from conventional light-sensitive materials like silicon because of perovskite's significant ionic properties. These properties are also a limiting factor for long-term stability, due to the low activation energy required for ion migration in the perovskite material. Ion migration has been found to accelerate after exposure to light or thermal stress [7]. Because of differences in activation energies for ion migration to happen between different parts of the perovskite structure, the halide anions and organic cations move more easily than heavy metal cations. Halide ions are the most mobile ones of the three, which is one of the main reasons for phase separation in mixed-halide perovskites [13].

In the case of $MAPbI_3$, it has been reported that the key photoinduced degradation occurs via iodide migration, in which light-induced decomposition of the Pb-halogen bond leads to structural instability. The I^- ion transition has the lowest activation energy (E_a=0.58 eV) compared to MA^+ (E_a=0.84 eV) and Pb^{2+} (E_a=2.31 eV), which originates from the proximity of I^- to the vacant sites at the edges of $[PbI_6]^{4-}$ octahedron [30]. The I^- ion is one of the key components in the reactions shown in equations 8-11, which causes the irreversible degradation of the films.

Another mechanism for degradation is ion migration of MA^+, which creates vacancies in the perovskite crystal structure. These vacancies alter the Pb-I-Pb bond angle, ultimately leading to distortions in the crystal structure and the formation of PbI_2 [28]. This organic cation movement is relatively slow, taking an hour or more to complete, compared to halide migration, which can occur within minutes under illumination. While these processes seem detrimental to the films' effectiveness, they are reversible after being stored in the dark for long enough. Although in the case of reactions with charge transport layers in complete devices, the degradation can be irreversible [13].

2.4 Air / oxygen

Oxygen molecules or atoms present in ambient conditions are one of the key species that degrade perovskite materials [31]. For example, $MAPbI_3$ is prone to degrade rapidly in oxygen-abundant environments, since the MA^+ can react with oxygen, generating charge barriers [15]. The exact oxidation mechanisms affecting perovskite thin films are still somewhat unclear. The oxygen-induced degradation in OIHPs has been investigated in numerous studies, and it has been suggested that oxygen molecules can only physisorb on the $MAPbI_3$ surface and that degradation occurs primarily under the influence of energy derived from light [31]. Even though this mechanism is not unanimously proven to be true, it is widely recognised that light illumination accelerates the degradation processes and enables certain reactions to happen [15,31]. This most likely happens due to activation of the photoactive layers in the $MAPbI_3$ surface, which leads to oxygen diffusion into the lattice [32]. Due to the different types of oxygen-induced degradation mechanisms in the presence or absence of light, they are discussed separately in the following chapters.

2.4.1 Dark conditions

It has been found that atmospheric oxygen alone can react with $MAPbI_3$ in dark conditions to some extent, which can be shown via the following equation:

$$4\,CH_3NH_3PbI_3(s) + O_2(g) \rightarrow 4\,PbI_2(s) + 2\,I_2(s) + 2\,H_2O(l) + 4\,CH_3NH_2(g). \quad (12)$$

Yet this reaction is thermodynamically unfavourable and has an enthalpy of +1.60 eV per O_2 molecule, indicating its significant acceleration upon light exposure [13].

Another variation of the common $MAPbI_3$ is the $MAPbBr_3$, which shows a very similar type of degradation in the presence of oxygen, indicating that the halide group has only a minor effect on the degradation caused by oxygen [15]. The possibility of degradation in dark conditions might be due to the strong oxidative properties of O_2 and its small molecular radius of 1.45 Å. These reactions also seem to be reversible and do not cause permanent degradation to the crystal structure, which is further evidence of the physisorption mechanism [33].

Tin (Sn^{2+}) based perovskite tends to suffer more oxygen-induced degradation compared to lead (Pb^{2+}) ones, even in dark conditions, due to high reactivity with oxygen [13]. The reason for high reactivity comes from the lower standard redox potential of tin, which is +0.15 V ($Sn^{2+}\rightarrow Sn^{4+}$) compared to +1.67 V ($Pb^{2+}\rightarrow Pb^{4+}$) of lead. This ultimately leads to the rapid oxidation of the Sn^{2+} ion to the more stable Sn^{4+} ion in ambient conditions [34]. Thermogravimetric analysis (TGA) results propose the possible degradation methods for $FASnI_3$ as follows:

$$2\,FASnI_3(s) + O_2(g) \rightarrow 2\,FAI(s/g) + SnO_2(s) + SnI_4(g). \quad (13)$$

Further issue with tin-based perovskite is the self-oxidation of $Sn^{2+}\rightarrow Sn^{4+}$, which can happen even without oxygen. This type of reaction results in the creation of Sn^{4+} compounds, like MA_2SnI_6 and SnI_4, that function as electron traps, lowering device efficiency and increasing non-radiative recombination [13].

2.4.2 Illuminated conditions

Li et al. [31] studied the impact of oxygen and charges in $MAPbI_3$ perovskites using density functional theory (DFT) computations and found that oxygen has weak interactions with pristine film surfaces and strong interactions with damaged ones, which is caused by the creation of superoxide (O_2^-) under light illumination [31]. The superoxide is generally formed due to the creation of electrons and holes by the photoexcitation of the perovskite material, which reacts with O_2 molecules [32]. The superoxide can then react and develop strong bonds with Pb and MA^+. The key insight of their study is the interplay between defects in the perovskite surfaces, atmospheric oxygen, and local charges. They emphasise the necessity of defect-free surfaces and positive local charges to prevent oxygen-induced degradation in $MAPbI_3$ perovskite [31].

Guo et al. [32] suggested in their analysis the possible degradation mechanisms of $MAPbI_3$ films under light illumination, in which the reactive superoxide (O_2^-) can deprotonate the MA^+, resulting in the formation of PbI_2, I_2, H_2O, and CH_3NH_2, which matches the chemical reaction shown in equation 12 with a regular oxygen molecule [32]. Another study made by Chi and Banerjee [15] reports that the anion vacancies have been identified as charge traps that promote the formation of O_2^- radicals. These vacancies are the primary sites in the lattice structure for reactions between oxygen and electrons, as illustrated in Figure 3 [15].

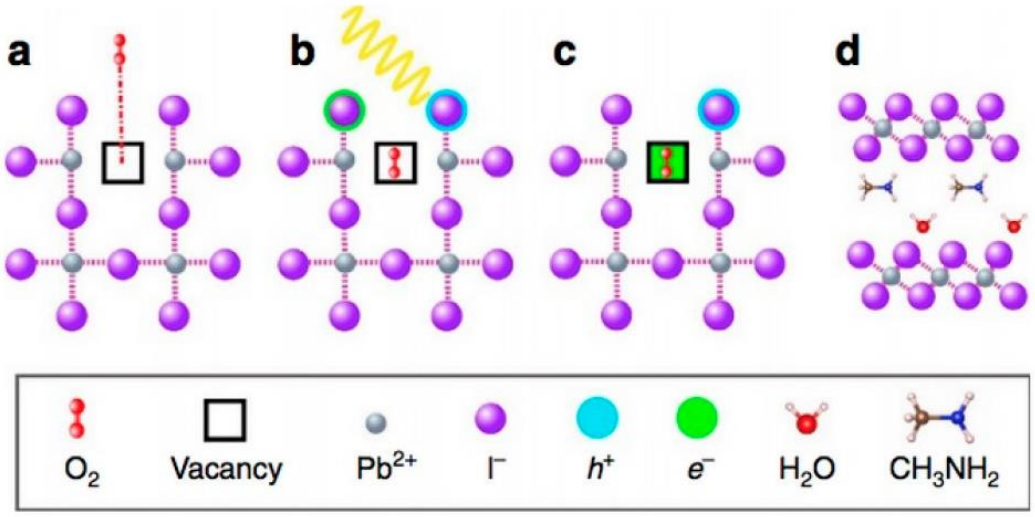

Figure 3. a)-c): Oxygen degradation mechanism of the $MAPbI_3$ perovskite via production of a superoxide. (Image reproduced with permission from [15]. Copyright 2021 American Chemical Society: Chemistry of Materials.)

In Figure 3, the different reactions are separated for easier understanding of the degradation mechanism. At first (a) the O_2 molecule infiltrates the perovskite lattice at a vacant site. Holes and electrons are then generated via photoexcitation of $MAPbI_3$ (b). Then the O_2 molecule captures the generated electron, forming the O_2^- (c). In the final state, the O_2^- deprotonation occurs, yielding the same final reaction products (d) [15]. This degradation mechanism further highlights the need for positive local charges and fewer vacancies in the perovskite lattice to prevent degradation from happening.

The superoxide has been found to accelerate the decomposition also by breaking the inorganic Pb-I bonds, which occurs due to the breakdown of the O-O bond and the subsequent formation of the O-Pb bond. This decomposition is further boosted when

the superoxide is reduced to peroxide (O_2^{-2}), as the double negative charge repels iodine anions and has a stronger affinity for lead cations [32].

Sharma et al. [35] studied the effect of air exposure on electron beam-induced degradation on perovskite films using transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), as well as optical measurements, and managed to separate the degradation process into 3 different phases. The phases can be shown as follows: Phases 1 and 2:

$$CH_3NH_3PbI_3(s) + O_2(g)\ or\ H_2O(l) \rightarrow PbI_2(s) + NH_3(g) + HI(g) + Z, \qquad (14)$$

where Z stands for organic residue, which contains compounds like CH_3NH_3I, $CH_3NH_2^+$, and CH_3I. In phase 3, the electron beam can further break down bonds in PbI_2, which can be written as:

$$PbI_2(s) \rightarrow Pb(s) + I_2(s), \qquad (15)$$

contributing to further creation of iodine and metallic lead in the perovskite material [35].

Atomic oxygen (O) can also be a factor for degradation in perovskite thin films, which can be generated by UV-induced photodegradation or other environmental photoreactions. The binding of atomic oxygen resembles exothermic behaviour with a very favourable incorporation energy of E_{inc}=-0.90 eV. Furthermore, the atomic oxygen can be positioned significantly closer to the lead ion, with a Pb-O bond length of approximately 2.28 Å rather than 2.46 Å distance with the O_2 molecule to the closest Pb ion, pointing to a chemical bond, which in turn suggests a detrimental effect of incorporating atomic oxygen into perovskite [33].

2.5 Combined environmental factors

The typical operating conditions for perovskite materials happen under the combined influence of extrinsic factors. These include heat, light, and surrounding air. Understanding the degradation mechanisms in these multi-stress conditions is essential for using perovskite materials in practice. Degradation with multiple factors tends to be synergistic and complex [13], and only a few examples are available.

Joo Yang et al. [36] studied the concurrent degradation mechanisms in mixed cation FA-based perovskites under harsh operation conditions according to the degradation protocol ISOS-L-3 explained in Figure 4 (a). The used materials consisted of $FA_{0.85}Cs_{0.15}Pb(I_{0.85}Br_{0.15})_3$ (FACs) and $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$ (FAMA) perovskites. In their study, they found that the degradation mechanisms between these two materials were completely different from one another. The FACs-based perovskite degradation begins in grain boundaries and PbI_2 crystals. As for FAMA perovskite, the degradation happens along its entire surface without regard to grains and boundaries between them as MA evaporates. Schematic presentation of degradation pathways is shown in Figure 4 (b).

XPS enabled the study of the different structural decomposition mechanisms between the two films. Based on the deconvolution analysis of the XPS peaks of perovskite and PbO, the FAMA perovskite is less resistant to oxidation than the FACs perovskite film. It was found that after 40 hours of testing, the majority of Pb^{2+} ions in the FAMA had been oxidised to PbO. The finding that FACs perovskite is more stable than FAMA perovskite was also concluded from scanning electron microscope (SEM) images and X-ray diffraction (XRD) [36]. SEM images of degraded perovskites can be seen in Figure 4 (c); the difference in material grain uniformity is clearly visible.

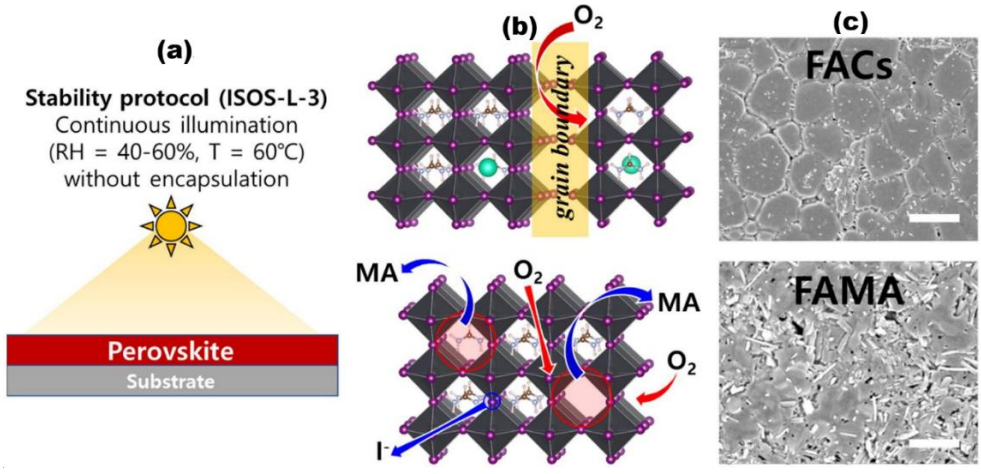

Figure 4. (a) Explanation of degradation protocol ISOS-L-3 parameters. (b) Schematic of the degradation pathways of FACs (above) and FAMA (bottom). (c) SEM images of perovskite materials after 20 hours of degradation. (Figure reproduced with permission from ref. [36]. Copyright 2022 Elsevier B.V.)

Another study conducted by Domanski et al. [13] on multi-stress induced degradation in perovskites found the order in which stress factors have the dominant influence

under varying conditions. For example, under low levels of humidity, oxygen has a greater influence in accelerating degradation compared to humidity, while at high levels of humidity, oxygen and water mutually reinforce each other in promoting degradation. In addition, they reinforce the fact that environmental exposure is a more significant factor than temperature alone in the degradation of perovskite materials, despite the lack of clarity about the precise mechanism at play under mixed conditions [13]. The assumption that thermal stress alone is not one of the major extrinsic degradation factors is supported by a study conducted by Salado et al. [37], where they observed certain levels of thermal stability in hybrid perovskite materials even at temperatures as high as 150 °C. Even though this stability must be compensated for upon exposure to other environmental factors [37].

3 Evaluation and characterisation of ageing

To understand the root causes of different mechanisms regarding the performance and degradation of perovskite materials, several characterisation tools must be used. These tools can evaluate the chemical, structural, morphological, and optoelectronic properties of perovskite materials [38]. Different characterisation tools for specific tasks are shown in Figure 5.

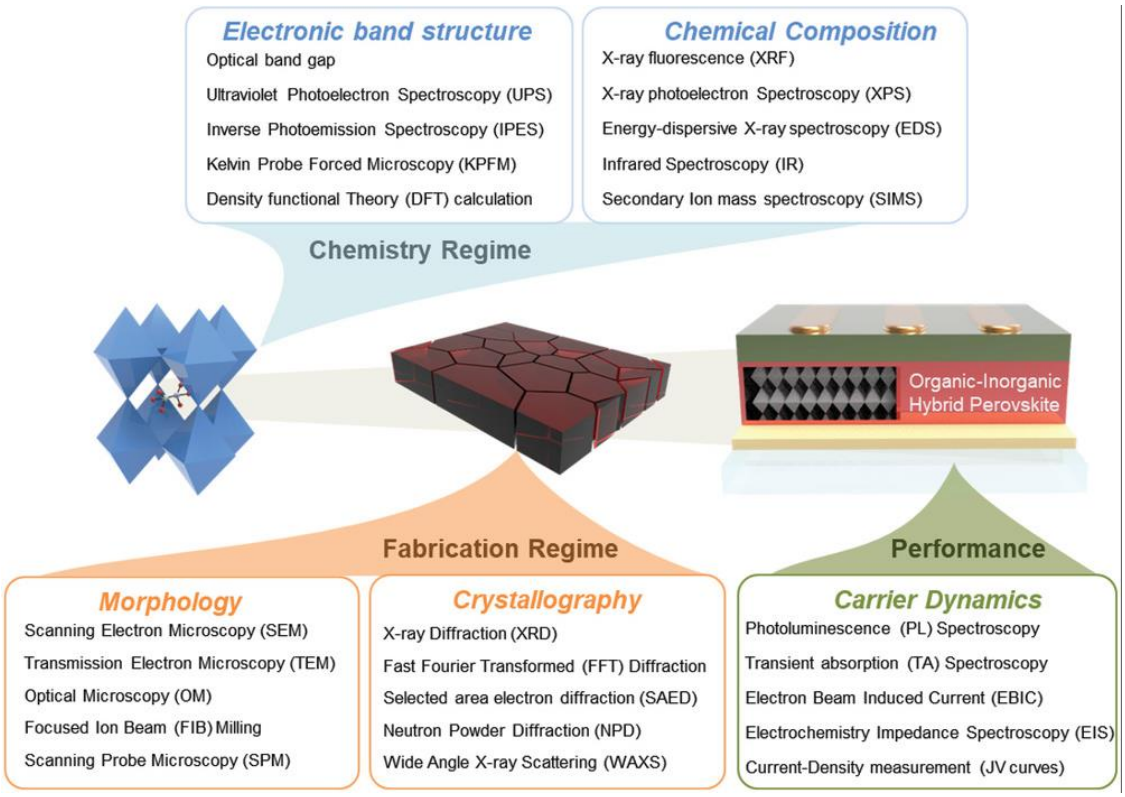

Figure 5. Summary of characterisation tools used in the PSC research field. (Figure reproduced with permission from ref. [38]. Copyright 2020 John Wiley and Sons/Wiley-VCH.)

Due to the unique characteristics of perovskite materials, such as photoinduced degradation, high dielectric constants, phase separation, and hysteresis, typical characterisation instruments from other photovoltaic technologies might lead to incorrect interpretations if used unmodified [38]. Typically, the characterisation can be done by either ex situ or in situ techniques, and the measurement methods used to study the degradation phenomenon are constantly evolving as new materials are being used [39]. Given the large number of different characterisation tools and methods used, only a selection is discussed here, to provide an overview of the degradation evaluation.

3.1 Structural stability and characterisation

The overall structural stability of ABX_3 perovskites is mainly determined by the crystal structure. A Goldschmidt tolerance factor (*t*) and its modified form by Bartel et al. can be used to predict the structure's stability via calculations using the ionic radii of the ABX components [39]. The Goldschmidt tolerance factor can be calculated as follows:

$$t = \frac{R_A + R_B}{\sqrt{2}(R_x + R_B)}, \tag{16}$$

where R_A, R_B, and R_X are the corresponding radii in the perovskite structure. The modified *t* is more complex and considers the oxidation state of the A cation and can be calculated as follows:

$$\tau = \frac{R_X}{R_B} - n_A\left(n_A - \frac{\frac{R_A}{R_B}}{\ln\left(\frac{R_A}{R_B}\right)}\right), \tag{17}$$

where τ represents the modified tolerance factor and n_A is the oxidation state of A cation [40]. According to Goldschmidt, the tolerance factor determines which crystal structure takes place in the formation of the perovskite, and they are listed in the following table 1 [39].

Table 1. Goldschmidt values and corresponding crystal structures [39].

***t* value**	**Crystal structure**
$t > 1$	Hexagonal or tetragonal
$0.9 < t < 1$	Cubic
$0.71 < t < 0.9$	Orthorhombic or rhombohedral
$t < 0.71$	No perovskite crystal structure

With the help of these calculations, it is possible to determine the prominent materials for each of the different sites in the ABX_3 structure for the best stability [40]. It is typically acknowledged that perovskite structures are formed when the *t* value is within the range of 0.71 – 1. For example, pure FA-based perovskite structures are too large according to the Goldschmidt tolerance factor ($t = 1.025$), and a non-photoactive phase is easily formed at room temperature [38].

Characterisation methods that use X-rays are useful tools for studying the perovskite materials and are largely used to analyse the lattice structure, chemical composition, and morphology. An X-ray source can also be utilised for in situ observations to see the changes in perovskite materials under different environmental stress factors, such as heat, light, or moisture, or different intermediate stages from creation to decomposition [40]. X-ray diffraction (XRD) is one of the key analysis methods used for degradation studies, and it works by the interference of monochromatic X-rays. The XRD method has the capability to show us the previously mentioned attributes, with crystallinity being one of the most crucial factors regarding efficiency and stability in PSCs [39].

Nalini V. et al. [33] show in their paper that $MAPbI_3$ thin-film degradation can be observed through microstructural changes in its diffraction patterns (Figure 6). The degradation can be observed as the presence of PbI_2 peaks after exposure to ambient air in the dark for 21 days [33].

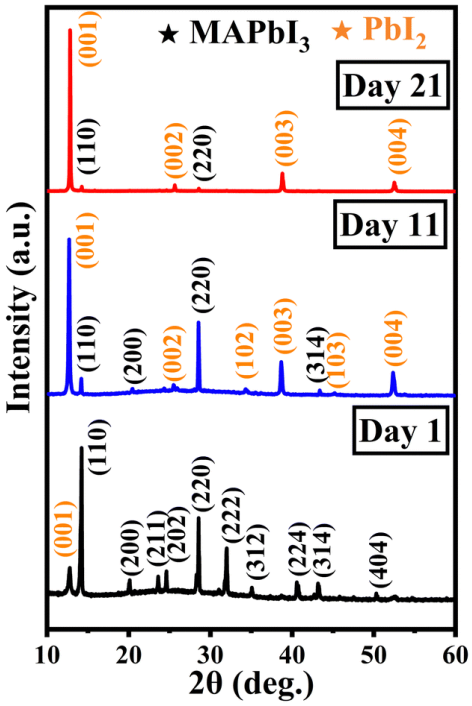

Figure 6. XRD patterns of $MAPbI_3$ thin films stored in ambient conditions for 1, 11, and 21 days in the dark. (Modified from Nalini V. et al. [33]. Copyright 2024 Nalini V. Published by The Royal Society of Chemistry: Materials Advances)

In Figure 6, the day 1 patterns indicating pure $MAPbI_3$ (black) are largely absent by day 21, and only a few very weak peaks (110 and 220 orientations) remain, indicating the degradation of the original material. While $MAPbI_3$ decomposes over

time, the orange peaks corresponding to the stable inorganic PbI_2 can be seen to grow, indicating it to be the main reaction product. Thus, further proving the PbI_2 to be the main degradation product of $MAPbI_3$ thin films [33].

Another method for chemical composition characterisation is time of flight secondary ion mass spectroscopy (ToF-SIMS), which also has the capability for 3D mapping of the degradation process in PSCs by the use of elemental depth-profiling [38]. In the ToF-SIMS method, the specimen is subjected to sputtering by a primary ion beam, which generates secondary ions that provide precise details about its chemical composition. This type of method can be used to study degradation by various extrinsic factors and the specimens' phase segregation, ion transport, and surface characteristics [41].

ToF-SIMS analysis was conducted on $MAPbI_3$ film that was annealed at 140 ◦C after casting. The mass spectra are divided between positive and negative secondary ions and can be seen in Figure 7, where the discovery of large, high mass atomic clusters in both spectra implies a thermal sputtering state [41].

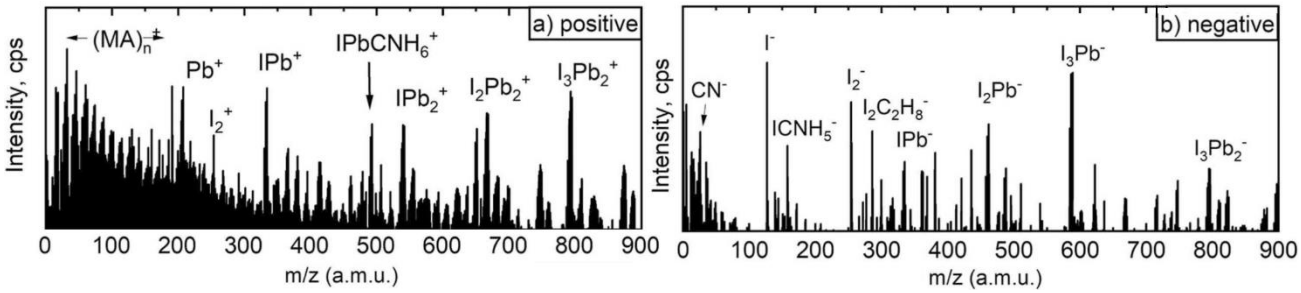

Figure 7. Mass spectra of $MAPbI_3$'s a) positive and b) negative secondary ions. (Modified from Díaz et al. [41]. Copyright 2024 Díaz et al., published by Elsevier: Synthetic Metals.)

The mass spectra show clear differences between different components of the ABX_3 structure. The inorganic lead and iodine, and their combination have large peaks in the negative ion spectra, while the organic parts (MA) of the structure are more present in the positive spectra. In accordance with expectations, the positive mass spectra also contain a considerable amount of Pb^+ and $IPbMA^+$ [41].

3.2 Morphological and microstructure analysis

The morphological and structural evolution of the perovskite films can be characterised using high-resolution electron microscopy (EM), which is one of the most widely used techniques in the study of materials. Scanning electron microscopy

(SEM) is typically used to characterise the morphology of micro-regions, and transmission electron microscopy (TEM) technology is used to characterise ultrastructure, which can provide illustrative information on the perovskite films subjected to stress [40].

SEM techniques offer high spatial resolution, up to 1-2 nm, which is possible due to the material being exposed to a highly energetic electron beam (ranging between 0.1-50 keV). The incoming beam interacts with the specimen and creates backscattered electrons, secondary electrons, and X-rays, along with phonon excitation in some circumstances. Images of these various events can be recorded with appropriate detectors, as the incident electron beam is typically scanned in the X-Y plane. In most SEMs, the secondary electron detector captures the topography of the specimen under examination at a magnification of 10-500 000 times and with a resolution of 1-2 nm [39].

SEM imaging was used to study the ageing of $MAPbI_3$ films at two different temperatures and under continuous light exposure in order to monitor the degradation process over different time periods (Figure 8) [29].

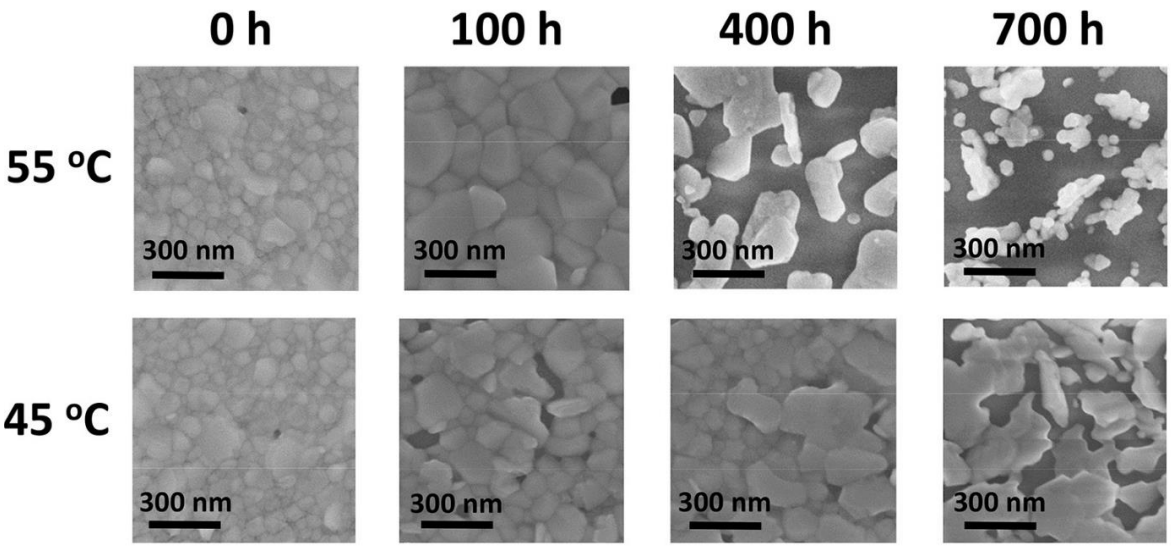

Figure 8. Top-view SEM images of $MAPbI_3$ films aged at 45 and 55 ◦C and under continuous light exposure for different time periods. (Figure reproduced with permission from ref. [29]. Copyright 2021 American Chemical Society.)

From Figure 8, the SEM images reveal clear differences in the surface morphology of the films at different temperatures over time. After 400 hours of ageing at a higher temperature (55 ◦C), the crystal structure and uniformity of the film are completely lost compared to film aged at a lower temperature (45 ◦C), which shows no clear

signs of degradation [29]. In addition, the annealing process can be monitored at the 100-hour mark at both temperatures, where the $MAPbI_3$ grains have grown from their original size.

TEM technology has exceptionally high spatial (lower than 1 Å), temporal (lower than 1 ms) and energy resolution (lower than 0.1 eV) [42] and can be used to study the specimen with higher magnification and resolution than optical or scanning electron microscopy. Yet the working mechanism is close to that of SEMs, where an electron gun emits an electron beam, but in the case of TEM, the emitted electrons pass through the specimen and are captured by a phosphor screen, which then creates an image with the specimen's details [39].

TEM has proven to be an essential characterisation technique when it comes to analysing the degradation of perovskites. Even though it can present certain limitations, since strong electron beams have been shown to damage the perovskites during TEM analysis. This problem originates from the photosensitivity of perovskite materials [39]. Due to this, the use of a low electron beam is always recommended for the characterisation of radiation-sensitive materials such as perovskites [38].

3.3 Optoelectronic characterisation

In situ optoelectronic characterisation is one of the valuable tools to discover the degradation mechanisms in perovskite films. These techniques can be used to obtain useful information on the development of carrier dynamics and the movement of ions because of exposure to heat, light, moisture, and electrical voltage [38]. In situ EM studies and X-ray analysis can both characterise the dynamic ion migration-based degradation mechanisms in perovskite devices, caused by the extrinsic factors and voltage effects. Nevertheless, this process must always be confirmed using other methods. However, the in situ optoelectronic methods allow for the direct characterisation of carrier dynamics and the evolution of ion transport during the decay process caused by the previously mentioned factors. Thanks to this, optoelectronic characterisation methods are used extensively to gain knowledge about recombination kinetics and the internal electrochemical potential for free charge carriers, directly from complete devices or individual perovskite absorption layers [40].

One of these optoelectronic characterisation methods is photoluminescence (PL) or its variation like, time-resolved photoluminescence (TRPL). These methods measure the number of emitted photons as a result of radiative recombination in semiconductors. In PL measurements, the peak intensity and its variation as a function of wavelengths give insight into the electronic structure of the cell and its recombination mechanisms. The motion of various carriers within the cell can lead to attenuation or amplification of the PL signal over longer time periods (seconds). In perovskite films or systems, a rapid decrease in PL intensity may indicate recombination, whereas a shift in PL intensity may indicate a change in bandgap. Making PL a valid tool for detecting these changes, which may be caused by stress factors leading to degradation of PSCs [39].

Another method for direct optoelectronic measurement is the Kelvin probe forced microscopy (KPFM), which can be used to map the local contact potential difference (CPD) or work function of the specimen under ageing [40]. The operating principle of the KPFM closely follows that of the atomic force microscope (AFM), yet it does not require contact with the specimen. It also has high spatial resolution, which enables a detailed investigation of the changes in electronic properties during device degradation at the nanoscale, as well as topographic data. A major challenge for the KPFM as a characterisation tool is the influence of temperature and humidity on the measurements [39].

AFM and KPFM analysis were conducted on $MAPbI_3$ thin films to study the work function in the perovskite crystals and morphological characteristics at two different annealing temperatures (140 ◦C and 160 ◦C). It was observed that the variations between surface potentials tend to increase as the surface disparity grows with higher annealing temperatures. The disparity between different surface morphologies can be seen from Figures 9a and 9b. The work function distribution map (Figure 9c and -d) reveals the local increases in the surface work function at certain points (grain boundaries) [41].

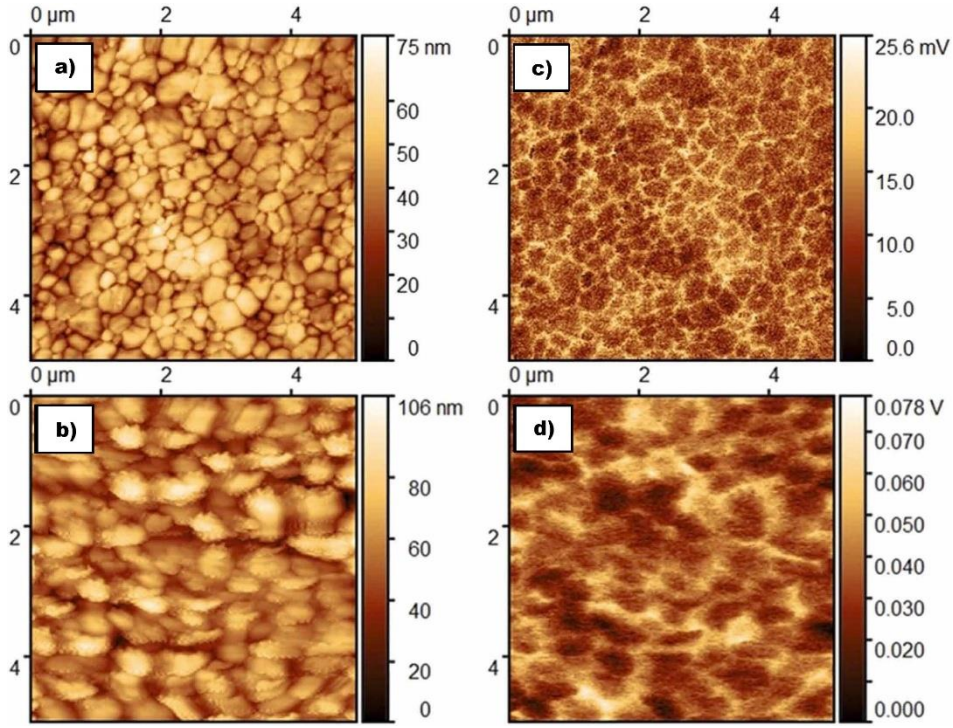

Figure 9. a)-d): AFM and KPFM images of $MAPbI_3$ thin films after annealing: a) Topograph after annealing at 140 ◦C. b) Topograph after annealing at 160 ◦C. c) potential distribution after annealing at 140 ◦C. d) potential distribution after annealing at 160 ◦C. (Modified from Díaz et al. [41]. Copyright 2024 Díaz et al., published by Elsevier: Synthetic Metals.)

A higher work function means a deeper Fermi level. The work functions on grain boundaries tend to be greater than those on the grains. This implies that the interfaces exhibit an electron transfer barrier due to an upward band bending in the equilibrium state, which is caused by differences in doping or defect distributions: The grain boundaries have more I^- vacancies and interstitial Pb^{2+} ions, whereas the grains have more Pb^{2+} holes and interstitial I^- ions. This supports the fact that the photovoltage is higher at grain boundaries than in the neighbouring grains, suggesting that the defects at the grain boundaries are shallow and that the mobility of carriers at the interfaces is greater [43].

4 Conclusions

The organic-inorganic hybrid perovskites with ABX_3 have emerged as prominent candidates for the photoactive layer in cost-effective and high-efficiency solar cells. Yet their instability due to various extrinsic and intrinsic factors that accumulate through multiple degradation pathways remains a major problem for their commercialisation. In this literature review, the effects of the four major environmental factors were investigated regarding their degradative properties on metal halide perovskites. The intrinsic factors, such as grain boundaries and ion migration, were also briefly examined.

The four major environmental factors included moisture (H_2O), thermal stress, light exposure, and oxygen. Among these, moisture-induced degradation is particularly critical, due to the naturally hydrophilic properties of commonly used perovskite materials, such as $MAPbI_3$. Water molecules interact with the perovskite via hydrogen bonds, triggering a complex degradation process that ultimately leads to the formation of PbI_2 and the release of volatile compounds. Thermal stress further accelerates this decomposition by destabilising the organic cation component, especially at high temperatures or during phase transitions.

UV- and visible light add complexity through photodegradation, which promotes ion migration, bond-breaking, and the formation of reactive species such as iodine and superoxide. Oxygen-induced degradation is highly dependent on light, but it can still occur to some extent in the absence of it. In both cases, degradation occurs primaly through oxidation reactions that are strongly linked to defect sites, and charge-carried dynamics, as well as oxygen’s natural properties. It is important to point out that these factors rarely act independently under actual operating conditions, and that their combined and synergistic effects significantly accelerate the degradation process.

Intrinsic factors such as grain boundaries, defect density, and ion mobility also play a decisive role in material stability. Grain boundaries can serve as primary sites for decomposition due to lower bond energies, which increases their sensitivity to chemical reactions. Ion migration (especially of halide ions) can cause severe phase segregation and structural instability under illumination. These intrinsic mechanisms

emphasise the importance of material engineering strategies, such as composition tuning and microstructure optimisation, for improving stability.

The evaluation and characterisation of perovskite thin film degradation require a combination of different techniques for a deep understanding of the underlying phenomena. Structural characterisation methods, such as XRD, provide information on phase transitions and crystallinity. Morphological studies using different electron microscopes (SEM and TEM) reveal microstructural evolution and degradation patterns. In addition, optoelectronic characterisation methods, including PL and KPFM, provide valuable insight into charge carrier dynamics and changes in electronic properties during ageing. The combination of in situ and ex situ techniques is important for characterising the dynamic nature of degradation processes. However, the sensitivity of perovskite materials to environmental conditions and measurement-induced damage creates continuous challenges for accurate characterisation.

Improving the stability of perovskite materials will require a diverse approach in the future. Advances in materials design are among the crucial ways to enhance resistance to extrinsic factors. A deeper understanding of degradation mechanisms under realistic operating conditions, including multi-stress testing, is also needed to narrow the gap between laboratory and practical applications. In the future, with sufficient research, PSCs have the potential to become a competitive and sustainable option in the global energy sector.

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