

Vibrational characterization of lead halide hybrid perovskites for optoelectronic applications

vorgelegt von

MSc. Mech. Eng. Josefa Fernanda Ibaceta Jaña,

an der Fakultät IV – Elektrotechnik und Informatik
der Technischen Universität Berlin
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Promotionsausschuss:

Vorsitzender: Prof. Dr. Steve Albrecht
Gutachter: Prof. Dr. Markus Wagner
Gutachter: Prof. Dr. Bernd Szyszka
Gutachter: Prof. Dr. Rodrigo Palma

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*"Differences of habit and language are nothing at all if our aims are identical and our
hearts are open"*
Albus Dumbledore

Abstract

FAPbI₃ is a hybrid lead halide perovskite used as absorber material in optoelectronic devices, especially in single-junction solar cells with efficiencies over 25%. Despite its outstanding properties, it degrades into a non-photoactive form in less than 24 h. The understanding of this material will support the design of optoelectronic devices. The main goal is characterize the vibrational spectra of hybrid lead halide perovskites. To this end, *FAPbI₃* single crystals were synthesized and measured by micro-Raman spectroscopy, following closely the degradation process and evaluating the mechanisms for phase transitions. Then, thin films were correlated with single crystals and characterized with X-ray diffraction to determine the effect of the annealing temperature on the material properties. At last, the impact of the variation of these properties in a p-i-n solar cell was investigated through a 1D simulation, leading to the implementation of a model that reproduces the experimental performance reported in literature specifying the current losses.

For the material characterization, single crystals were chosen due to the fewer defects compared to thin films. The attribution of Raman modes by Density Functional Theory led to three frequency zones according to the vibration source: I-octahedral modes, II-perovskite modes, and III-molecular modes. The study of zones I and II resulted in structural polymorphism, identification of a phase transition at 100°C, and attribution of a distorted cubic morphology at room temperature. Also, the structural instability was linked to the FA^+ rotation outside the molecular plane. From Zone III the absence of hydrogen bonds in hybrid lead halide perovskites was deduced. Additionally, it was concluded that the partial substitution of I^- by Br^- and FA^+ by Cs^+ in *FAPbI₃* breaks the lattice symmetry and hinders the critical molecular rotation.

The XRD pattern analysis of thin films showed different Pb-I bond lengths and phase composition, which were applied to a model varying the band-gap and bulk defect density. The simulation considers the secondary phases in the degraded material and interlayer of *PbI₂*.

The understanding of lead halide perovskites may bring additional assets in the development of new stabilization techniques and the design of the thin film deposition process to optimize the film quality. Even beyond, it may contribute to the design of new and stable structures for optoelectronic applications.

Zusammenfassung

$FAPbI_3$ ist ein hybrider Bleihalogenid-Perowskit, der als Absorbermaterial in optoelektronischen Bauelementen verwendet wird, insbesondere in Solarzellen mit Einzelübergang und einem Wirkungsgrad von über 25%. Trotz seiner hervorragenden Eigenschaften zerfällt es zu einer nicht-photoaktiven Form in weniger als 24 Stunden. Das Verständnis dieses Materials wird die Entwicklung von optoelektronischen Geräten unterstützen. Das Hauptziel ist die Charakterisierung der Schwingungsspektren von hybriden Bleihalogenid-Perowskiten. Zu diesem Zweck wurden $FAPbI_3$ -Einkristalle synthetisiert und mit Hilfe der Mikro-Raman-Spektroskopie gemessen, wobei der Degradationsprozess genau verfolgt und die Mechanismen der Phasenübergänge bewertet wurden. Anschließend wurden dünne Filme mit Einkristallen korreliert und mit Röntgenbeugung charakterisiert, um den Einfluss der Glüh-temperatur auf die Materialeigenschaften zu bestimmen. Schließlich wurde die Auswirkung der Variation dieser Eigenschaften in einer p-i-n-Solarzelle durch eine 1D-Simulation untersucht, was zur Implementierung eines Modells führte, das die in der Literatur berichteten experimentellen Leistungen unter Angabe der Stromverluste reproduziert.

Für die Materialcharakterisierung wurden Einkristalle gewählt, da sie im Vergleich zu dünnen Schichten weniger Defekte aufweisen. Die Zuordnung der Raman-Moden durch die Dichtefunktionaltheorie führte zu drei Frequenzonen entsprechend der Schwingungsquelle: I-oktaedrische Moden, II-Perowskit-Moden und III-molekulare Moden. Die Untersuchung der Zonen I und II führte zu strukturellem Polymorphismus, zur Identifizierung eines Phasenübergangs bei 100°C und zur Zuordnung einer verzerrten kubischen Morphologie bei Raumtemperatur. Außerdem wurde die strukturelle Instabilität mit der FA^+ -Rotation außerhalb der Molekülebene in Verbindung gebracht. Aus Zone III wurde das Fehlen von Wasserstoffbrückenbindungen in hybriden Bleihalogenidperowskiten abgeleitet. Außerdem wurde festgestellt, dass die teilweise Substitution von I^- durch Br^- und FA^+ durch Cs^+ in $FAPbI_3$ die Gittersymmetrie bricht und die kritische Molekülrotation behindert.

Die XRD-Musteranalyse der dünnen Schichten zeigte unterschiedliche Pb-I-Bindungslängen und Phasenzusammensetzungen, die auf ein Modell angewendet wurden, das die Bandlücke und die Bulk-Defektdichte variiert. Die Simulation berücksichtigt die sekundären Phasen im degradierten Material und die Zwischenschicht aus PbI_2 .

Das Verständnis von Bleihalogenid-Perowskiten kann zusätzliche Vorteile bei der Entwicklung neuer Stabilisierungstechniken und der Gestaltung von Dünnschichtabscheidungsprozessen zur Optimierung der Schichtqualität bringen. Darüber hinaus kann es auch zur Entwicklung neuer und stabiler Strukturen für optoelektronische Anwendungen beitragen.

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Chapter 1

Introduction

The decarbonization of the energetic matrix is one of the most critical tasks nowadays. The global warming phenomenon has shortened the time frame to come up with innovative solutions for the industry and requires the immediate application of green technologies. For several years, the potential of solar energy has been explored via thermal systems and photovoltaic solar cells. From the preceding ones, one of the innovations that show the most promising results is the perovskite solar cell, which, from the initial development in 2009 by Kojima et al[56], has increased its efficiency from 3.8% to 26%. Lead Halide Perovskite (LHP= $APbX_3$) is a photoactive material composed of an arrangement of PbX_6 octahedra surrounding a cation that is an organic molecule in the hybrid compounds. This cation was at the beginning methylammonium ($MA^+ = CH_3NH_3^+$) but it was later replaced by formamidinium ($FA^+ = (NH_2)_2CH^+$) due to its narrower bandgap and improved thermal stability. LHPs possess impressive optoelectronic properties that explained the adequacy in solar cells such as sharp absorption edge, high absorption coefficients, the large diffusion length of free charge carriers, and low recombination rate. The principal challenges are toxicology, stability, low reproducibility, scalability, and high prices of the devices.

In particular, formamidinium lead iodide ($FAPbI_3$) thin-film solar cells have achieved record efficiencies, over 26%. However, it presents a structural instability: a phase transition from the photoactive α -phase into a non-photoactive δ -phase in less than a day when is stored in ambient air. The material is considered degraded to the device application. Even though several strategies were employed to enhance the stabilization, e.g., compositional engineering and surface passivation, there is a non-consensus in the literature about the physics of the transitions and the material morphology.

Hence, in this thesis, the vibrational spectra of $FAPbI_3$ and other LHPs are characterized under thermal and compositional treatments. Optoelectrical properties in films are determined for application in thin-film devices.

This thesis is structured as follows:

Chapter 2 presents a short review of the literature related to materials and devices studied in this thesis. In particular, the morphology of LHPs, Raman spectroscopy, and performance in thin-film optoelectronic devices.

Chapter 3 explains the experimental methods employed, from the sample synthesis to the characterization techniques.

Chapter 4 presents the results. It is divided in five parts. *Chapter 4.1* attributes Raman modes for the $FAPbI_3$ spectrum based on Density Functional Theory. *Chapter 4.2* determines the polymorphism at room temperature (RT). Raman spectra of the sample as-synthesized, degraded, and thermally recovered were analyzed. The Raman modes vary in frequency and intensity. Furthermore, temperature-dependent measurements show variations that are added to thermal expansion effects. Mechanisms of degradation into the non-photo active structure are proposed. *Chapter 4.3* proves the absence of hydrogen bonding in hybrid LHPs. To that end, we performed temperature dependence Raman spectroscopy on FAI salts and $FAPbBr_3$ and $MAPbBr_3$. A comparison was made between the analyzed samples and the iodide analogous at RT. After considering chemical and physical principles, we determined that the interaction does not contribute charge transfer and therefore is not directional. *Chapter 4.4* analyzes mixed perovskites based on $FAPbI_3$. The influence of the additional atoms, Cs^+ , and Br^- , was identified in the Raman spectra and related the differences to the structural stability. The attribution of Raman modes of FA^+ compounds was made through the computational simulation of $FAPbI_3$ Raman modes. *Chapter 4.5* determines the effect of the annealing temperature in thin films regarding the composition and structure of each state of $FAPbI_3$. A sensitivity analysis is performed in simulated solar cells devices regarding these parameters.

Chapter 5 summarizes the findings of this thesis and presents suggestions for future research.

The main findings of this thesis are:

- **Determination the $FAPbI_3$ structure.** The material presents a distorted cubic geometry at RT, undergoing a phase transition into the perfect cubic organization around 100°C.
- **Characterization of the polymorphism.** Four polymorphs have been identified at room temperature, from where three are photoactive. They differ in the lattice constant, level of distortion, PL signal, and stability.
- **Proposal of a degradation mechanism of $FAPbI_3$.** The degraded sample contains three regions: α_δ , δ and transition. A structural instability mechanism is proposed.
- **Analysis of the interaction of the organic molecule FA^+ and the inorganic framework PbI_6 .** Hybrid LHPs do not present hydrogen bonds. A direct consequence is to discard this bond as a cause of structural stability.
- **Evaluation of the impact in the Raman spectrum of the addition of Cs^+ and Br^- into $FAPbI_3$.** Appearance of additional modes is related to cation coordination and symmetry break. These are critical factors in the enhancement of structural stability.

- **Determination of the influence of annealing temperature in $FAPbI_3$ thin films and the impact in optoelectronic applications.** Annealing temperatures higher than the phase transition temperature generate lower content of PbI_2 in exchange for higher local defects. Below that temperature, smaller cell sizes are obtained which are more beneficial to device performance.

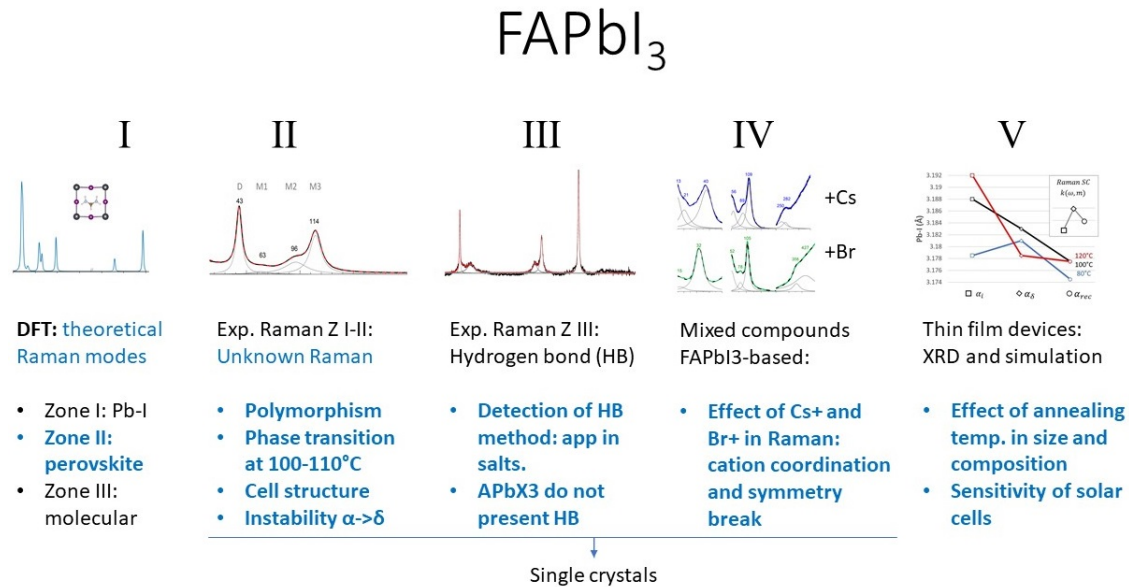


Figure 1.1: Results highlights. Novel measurements and conclusions are denoted in blue.

Chapter 2

Literature Review

This section covers the state of the art of LHPs, particularly $FAPbI_3$. *Chapter 2.1* refers to the structural properties while *Chapter 2.2* to the optoelectronic properties and applications. Fundamentals of semiconductors and devices are detailed and explained in classic books [96, 115]. The physics regarding Raman spectroscopy, the main characterization tool of this thesis, can be found in the book of Ferraro [29].

2.1 Structure of Lead halide Perovskites

2.1.1 Morphology

The perovskite structure is usually expressed as ABX_3 [36, 118], where the cation A is occupied in a cube-octahedral site and the cation of B is occupied in an octahedral site, accompanied by 6 anions X, as BX_6 , which forms a 3D structure linked from the corners. The ideal cubic structure of perovskites ($Pm\bar{3}m$) is shown in Fig. 2.1, where is it exemplified with $FAPbI_3$.

The components are restricted in size to keep the lattice parameters of the structure, that is why only selected combinations are used for different applications. For example, MA^+ , FA^+ , and Cs^+ are used for the A-site cation, Pb for the B-site, and I and Br for the X-site. Goldschmidt tolerance factor is used in perovskite to indicate the stability and distortion of crystal structures by considering the components as spheres in contact and regulating the size to fit in the interstices [36]. It is translated into the next equation:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (2.1)$$

In this, $r_i, i = \{A, B, X\}$ represents the ionic radius of the selected component. For lead halide perovskite, formability is expected in a range of $0.813 < t < 1.107$ [66]. For $t > 1$, cation A ionic radius is bigger than Pb and the resulting structure may be hexagonal. For

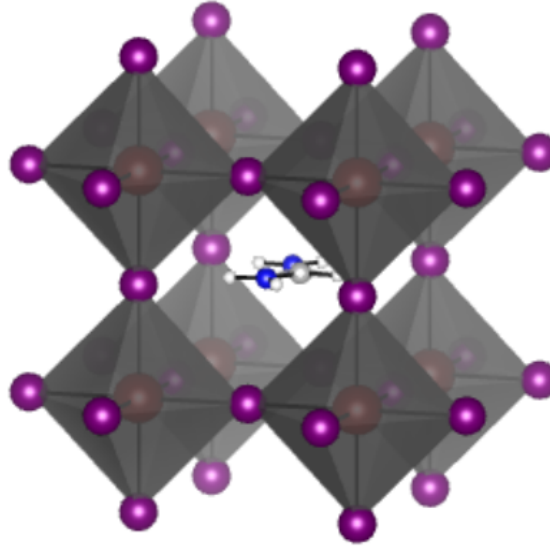


Figure 2.1: Cubic perovskite 3D structure, $FAPbI_3$. Red spheres correspond to Pb, purple to I, blue to N, gray to C and white to H.

$t = [0.9 - 1.0]$ it is expected a cubic structure, being $t = 1$ the ideal value. For values less than $t = 0.9$, the structure may be orthorhombic or rhomboidal because the cation A is too small to fit in the interstices of Pb [36]. The structures can also present an octahedral distortion characterized by a tilt. This tilt can be parallel to a crystallographic axis, have different amplitude, and be in phase or anti-phase with the surrounding cells tilts [40, 41].

Table 2.1 shows the atomic mass and ionic radius of the studied components and tolerance factors of perovskites used in the further analysis. The ionic radii of cations Cs^+ , MA^+ and FA^+ were determined in the work of Amat *et al.* [4], Jishi *et al.* [51] and Nazarenko *et al.*[85], respectively, while the ionic radii of metals are from the work of Park *et al.*[91]. The tolerance factors were calculated with the presented values and in case of the mixed perovskites, with a pondered mean value for each component according to the species contribution. Cell structures of $MAPbI_3$ and $MAPbBr_3$ are extracted from the work of Leguy *et al.*[65], $FAPbBr_3$ by Perumal *et al.* [95], $CsPbBr_3$ by Hirotsu *et al.* [46] and $CsPbI_3$ by Stoumpos *et al.*[112]. The structure of $FAPbI_3$ is still a matter of discussion in literature, however, the general consensus is cubic $Pm\bar{3}m$ or $Im\bar{3}$.

Table 2.1: Ionic radii [4, 51, 85, 91] and atomic masses of perovskite components and tolerance factors and cell structures of perovskites crystals [46, 65, 95, 112].

Material	Atomic Mass (u)	Ionic Radius ($\text{\AA}$)	Perovskite	Tolerance factor	Cell Structure
MA^+	28.0	2.23	$MAPbI_3$	0.924	Tetragonal $I4/mcm$
FA^+	46.0	2.53	$MAPbBr_3$	0.941	Cubic $Pm\bar{3}m$
Cs^+	132.9	1.81	$FAPbI_3$	0.987	Cubic
Pb^{2+}	207.2	1.19	$FAPbBr_3$	1.008	Cubic $Pm\bar{3}m$
I^-	126.9	2.20	$CsPbI_3$	0.834	Orthorhombic $Pnma$
Br^-	79.9	1.96	$CsPbBr_3$	0.846	Orthorhombic $Pnma$

According to the Goldschmidt factors presented, the studied HPs should be all cubic, with some distortions demonstrated by non-ideal 1.0 values. Since we admitted a spherical shape of the A cation, which is not the case for organic chains, the tolerance factor is considered a comparative criterion. According to it, FA^+ fits into the PbI_6 grid very well, providing compactness with negligible deviation from the ideal cubic symmetry. In reality, however, FA^+ does not represent a sphere but has an oriented position. A representation of the surrounded cations is presented in Fig.2.2, showing the orientation of the octahedra in the lattice.

The cell structures of the studied materials are presented in Fig.2.2, indicating the orientation of the octahedra in the lattice. The ideal cubic $Pm\bar{3}m$ the structure possesses no acknowledgeable distortions, as is the case of $MAPbBr_3$. In this, the PbI_6 framework has a O_h symmetry. On the contrary, the larger iodide generates an elongated tetragonal structure when used in MA-based LHPs. This directed distortion of the octahedron is balanced by the organization of the adjacent cages. Similar is the case of cubic $Im\bar{3}$, in which the distortion is correct to adjust the lattice length in all directions. The small Cs^+ leads the surrounding cages to shrink and expand in opposite direction, organizing the structure in an orthorhombic fashion.

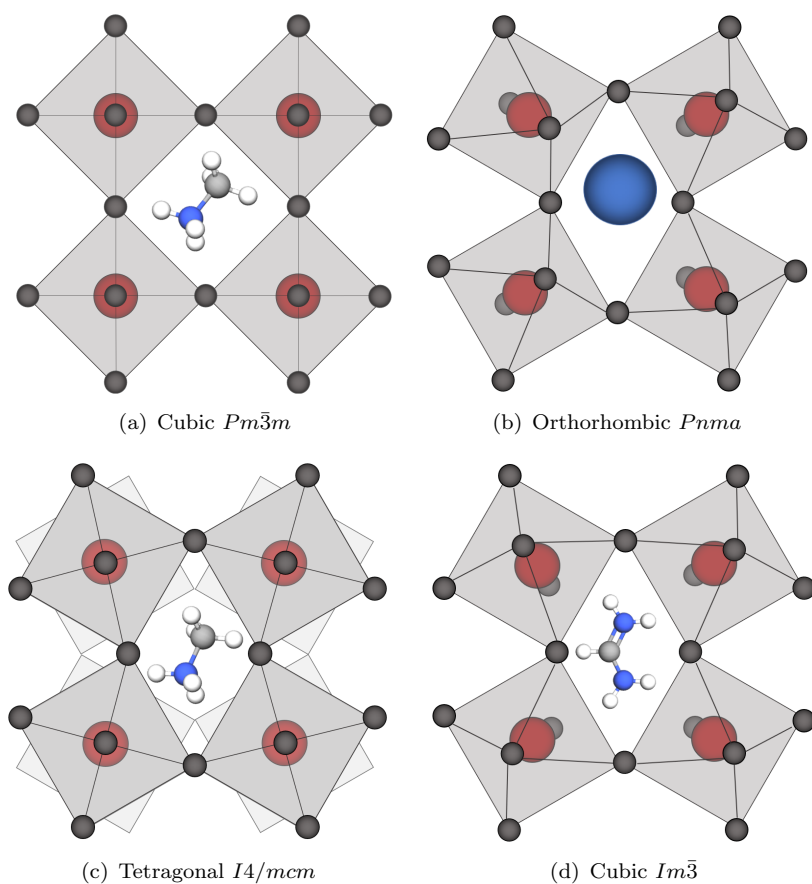


Figure 2.2: 2D non-scale representation of octahedra orientation in the lattice. Red spheres represent Pb; grey, halide; and blue cation, Cs^+ .

2.1.2 Phase transitions

The crystalline structures depend also on temperature, presenting different organizations according to their vibrational modes. As perovskites are highly dynamic, the fluctuation among different structures defined a specific structure on average, which makes phase transitions smooth [101]. The phase transitions of the studied single component perovskites in the range studied are presented in Fig. 2.3 [28, 65, 76, 108, 111, 112].

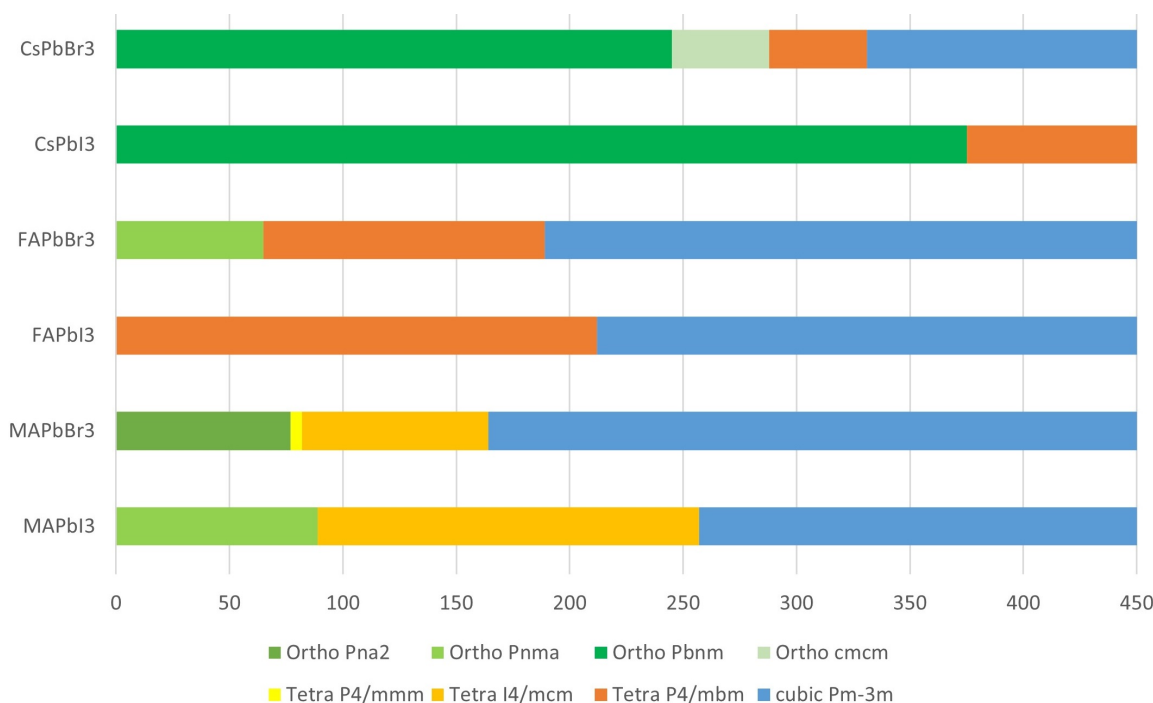


Figure 2.3: Phase transitions of perovskites between 0 and 450 K. Orthorhombic phases are depicted in green, tetragonal in yellow or orange, and cubic in blue.

At low temperatures, crystals have an orthorhombic structure and with the increase of energy, molecules and atoms vibrate to achieve a tetragonal and then cubic organization. In $MAPbI_3$, a smooth transition from tetragonal $I4/mcm$ to orthorhombic $Pna2$ occurs in a small temperature window (5°C), which is determined as tetragonal $P4/mmm$ [65]. Due to the high compactness of $FAPbI_3$ the lowest symmetry that reaches this temperature range is tetragonal $P4/mbm$, which is closer to the cubic symmetry than the previous phase [28]. In the case of $CsPbBr_3$ and $CsPbI_3$, the low compactness of the structure results in an orthorhombic organization for the whole range of temperature [112].

2.1.3 Organic cations

The electronic spherical symmetry of the perovskite ions allows the crystal to organize compact [105]. The organic cations MA^+ and FA^+ are to some extent polar. MA^+ cation represents a kind of soft and large proton, with a positive charge delocalized around nitrogen due to the donor-acceptor interaction (see Fig.2.4a). FA^+ has an even higher degree of the proton charge delocalization, namely between two nitrogen atoms (see Fig.2.4b). At the

same time, the N-C-N chain becomes bent due to the proton embedding, with an inter-atomic angle of 125° [88]. Resonant stabilization of the FA^+ structure is responsible for the low dipole moment ($0.21D$) as compared to MA^+ ($2.29D$) [34]. Since FA^+ is larger being at once a weaker dipole, it possesses a slower molecular reorientation than MA^+ [6, 129], revealing a lower frequency. MA^+ time constants are 0.3 ps for the wobbling in a cone 3 ps for 90° jumps, in contrast with the 2 ps single roll-over process of FA^+ .

It is worth noticing that the deformations of a Pb-X framework perform as polarons in HPs. The formation time of polarons is then dependent on the cation utilized [83]. This in combination with the absence of trap-site defects, provides outstanding optoelectronic properties [78].

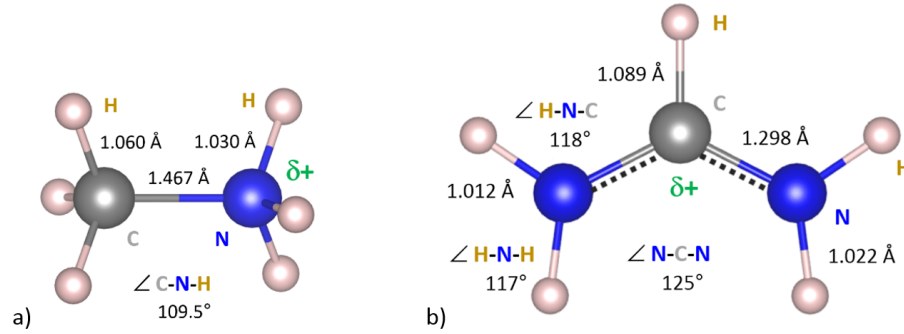


Figure 2.4: Chemical structure of cation in A-site, a) MA^+ and b) FA^+

As can be appreciated in Fig. 2.4, MA^+ and FA^+ present indeed different spatial dispositions, from 3D to 2D respectively [97]. A size comparison of the studied cations is presented in Fig. 2.5, in which the green portion of the spherical model represents the vacuum used by the organic chains to rotate and stretch.

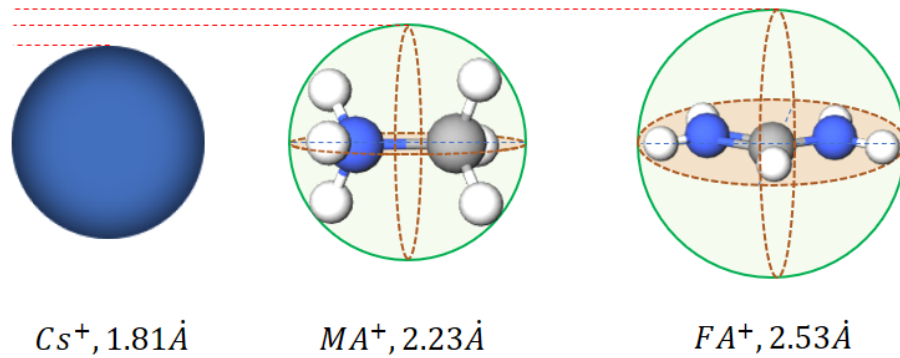


Figure 2.5: Spherical representation of cations, size comparison.

The strength of chemical bonds between atoms in the structure should be considered [105]. The crystalline structure is made of metals except for the cation in the A-site in the case of MA^+ and FA^+ ; therefore, metallic atoms are joined together by overlapping their external orbitals, sharing valence atoms. The compactness of the structure determines the strength of the bond, being the ideal centered cubic. The atom in the A-site shares an electron that is included in the balance, remaining as a $1+$ cation. Cs^+ is a metal, so the structure only contains metallic bonds and it is better organized; MA^+ presents a single polar covalent bond, and an electron is donated by the nitrogen atom to form three hydrogen bonds

and one carbon-nitrogen bond (see Fig.2.4a); FA^+ has hydrogen bonds and a delocalized electron between carbon-nitrogen, creating a double bond in any of these interactions and consequently, a stronger union to the structure (see Fig.2.4b).

2.1.4 Inter atomic bonds

Three types of interactions exist in LHPs: (i) within the inorganic octahedra, (ii) within the molecule, and (iii) the interactions of both aforementioned. The first and third ones are already determined. The inorganic octahedra are formed by ionic bonds while within the molecule atoms are joined by covalent bonds. The interaction between the organic cation and the inorganic framework remains debatable. Hydrogen bonds are widely admitted to exist in LHPs. In this manner, they are attributed to be responsible for surface passivation [81], structural stability of the mixed cation compounds [4], structural instability of $FAPbI_3$ [28, 122, 129, 141], ferroelectric behavior [130], enhanced carrier diffusion length of $MAPbI_3$ [34], among others.

Since LHPs are the salts with ionic interaction between organic and inorganic constituents, hydrogen bonds are uneasy to evidence neither by computational nor by experimental methods. Most judgments presented in the literature for LHPs are indirect. Applying DFT, the bonding energies [64, 119] and bonding distances [4, 100] were calculated that resulting in the recognition of hydrogen bonds. Experimentally, the presence of H-bonds was justified using critical bonding distance, i.e., the sum of the corresponding Van der Waals radii of the involved atoms. These data could be obtained from neutron diffraction patterns [129], solid-state 1H nuclear magnetic resonance [81, 114] and from shifting of vibrational modes in Infrared and Raman spectroscopy [39, 65, 81, 86, 103, 123, 131].

Hydrogen bonds play a crucial hidden role in our water-based world and living organisms in particular. Despite the individual weakness, their collective impact stipulates the organization of polypeptide chains and determines the mechanisms of enzyme catalysis [23, 30, 121]. Often the packing of organic molecules in crystals is influenced by hydrogen bonds [44, 145]. By definition, the hydrogen bond is a dipole-dipole attraction between a hydrogen atom bound to a strongly electronegative atom and therefore having an effective positive charge and a third-party strongly electronegative atom. Due to the relative weakness, it is non-trivial to characterize these bonds. Formally, their existence can be admitted if the distance between interacting dipoles (molecules) is lower than the sum of their Van der Waals radii; and if some charge transfer occurs between dipoles (molecules). In many cases hydrogen bonds are revealed via the deformation of molecules or molecular chains [35, 57].

The bonding force is partially determined by the dipolar moment of the molecule. Geometrical factor also determines the strength: the opposite effective charges (δ^- and δ^+) should locate as close as possible. It is hard however to evaluate any given situation about the Van der Waals radii as their determination involves a high degree of uncertainty. Indeed, molecules do not represent compact spheres like ions typically do. In literature, it has been even proposed to discard this criterion in judgment on hydrogen bonds [107].

A hydrogen bond can be described as a quantum resonance between a neutral state ($\Phi_0 : -X-H...X$) and a charge transfer state ($\Phi_1 : -X-H^+...X^-$) [2]. In Raman spectroscopy,

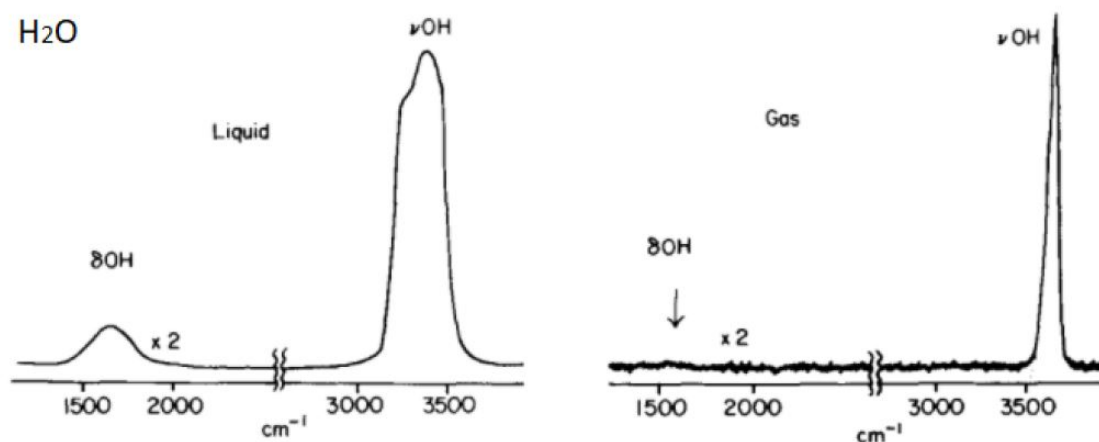


Figure 2.6: Raman spectra of H_2O in liquid and gas phase [2]. License for reproduction in Annex

the Φ_1 state appears as an additional mode whose intensity depends on the strength of the bond: For weak interactions, it is low, whereas for strong ones it can be as intense as the Φ_0 related mode. This last is for instance the case of liquid water. The Φ_1 related peak can be red or blue-shifted concerning the Φ_0 peak that is determined by the nature (bonding or antibonding) of the available acceptor (X - H) molecular orbital. An additional peak may appear for the stretching modes of a donor group, and it may be also coupled with a decrease in the intensity of the bending modes. This consideration has been proven to explain the situation in various molecules and solutions [2, 26]. Figure 2.6 shows a representation of the criterium of charge transfer. In liquid water, the presence of hydrogen bonds results in an additional peak of the stretching mode, while the bending mode increases its intensity.

2.1.5 Raman spectroscopy

Raman Spectroscopy is a non-destructive chemical analysis technique based on light scattering, which made it suitable for sensitive samples. It gives information about chemical structure, phases, polymorphism, defectiveness, and molecular interactions.

When light is scattered by matter, almost all the process is elastic, i.e., it has the same frequency as the incident light (Rayleigh). However, a small portion of the scattering is inelastic (ca. $10^{-6}\%$). The cloud of electrons in the matter is distorted by the incident light and creates a virtual state. This state is not stable and a photon is radiated. The electron can be excited from the ground state into a vibrational level that involves energy absorption (Stokes), or it can be excited from a vibrational level to the ground state (anti-Stokes), which involves energy transfer to the scattered photon. A scheme is presented in Fig. 2.7.

A Raman spectrum presents Lorentzian peaks, which are related to Raman modes. These modes can be simplistically understood under the harmonic oscillator model, $\omega = \sqrt{k/m}$ [128]. This model is the solution of the Schrödinger equations that describes the atomic vibrations in a system. For a simple scheme, in a diatomic molecule the frequency of the vibration " ω " depends directly on " m ", which represents the reduced mass, and " k ",

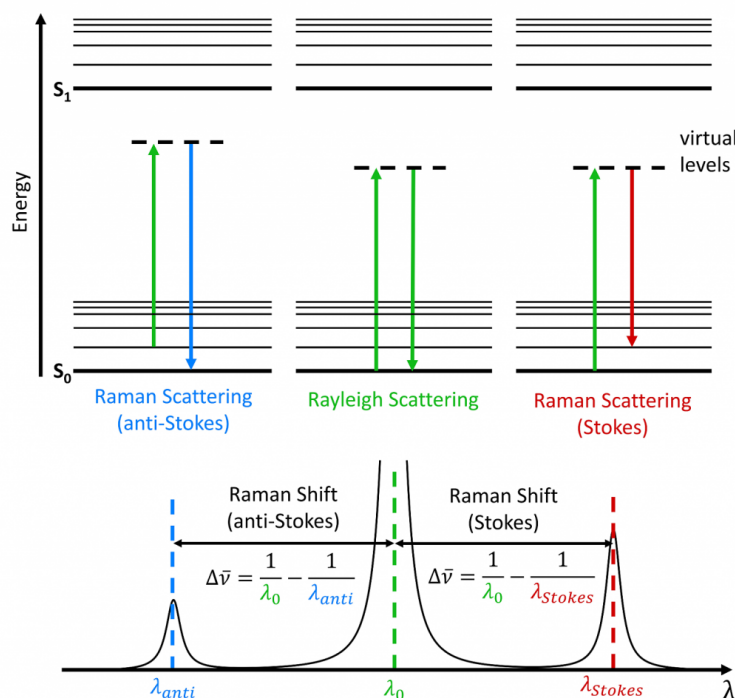


Figure 2.7: Jablonski Diagram showing the origin of Rayleigh, Stokes and Anti-Stokes Raman Scatter [1]

which represents the spring constant, which is related to the strength of the chemical bond between the involved atoms.

In the spectrum, each peak corresponds to a specific molecular bond vibration, including individual and group bonds. There are four parameters to consider in the peak analysis:

- **Position:** it denotes the molecular structure.
- **Height:** it is related to the substance concentration that is vibrating in such mode.
- **Width:** it is related to the material defectiveness. The mode has a sharp peak for highly crystalline structures.
- **Shift:** It can be red or blue, i.e., to lower or higher frequencies. Redshift denotes tensile stresses while blue shift, compressive ones.

The activation of Raman modes depends on the variation of the polarizability ellipsoid of a structure or molecule. It is often described as the shape of the electron cloud. When light interacts with the polarizability ellipsoid, it may cause an oscillating induced dipole which distorts the electron cloud. In this way, symmetric stretches, vibrations of multiple bonds or heavy atoms, are normally accompanied by strong Raman bands.

Raman spectroscopy has already disclosed the lattice dynamics for some LHPs. The experimental Raman spectra of LHPs have been supported with Density Functional Theory (DFT) calculations only for $MAPbI_3$ [65]. The interesting range of the vibrational spectrum of $MAPbX_3$ compounds is $10\text{-}3200\text{ cm}^{-1}$ where the most pronounced peaks are correlated

to the motion of the PbX_6 octahedra and the reorientation of the MA^+ cation. These peaks appear in the spectra below and above 200 cm^{-1} , respectively[43, 63, 65, 86]. Dynamic disorder of MA^+ causes the splitting of independent harmonic modes, resulting in a larger number of Raman peaks at high frequencies[65]. The variation of halogen in $MAPbX_3$ shifts the Raman peaks in accordance with the Pb-X bond strength[63, 86].

There are experimentally measured Raman spectra for $FAPbBr_3$ and $CsPbBr_3$ until 3500 cm^{-1} and 320 cm^{-1} , respectively, but the specific modes have not been ascribed for the whole spectrum [18, 43, 123, 132]. For $FAPbBr_3$, the attribution is well-made for molecular modes ($> 500\text{ cm}^{-1}$), associating them with the Raman modes of the isolated FA^+ molecular ion [60]. For $CsPbBr_3$, a general description of modes was done on the basis of atomic trajectories, which reveals that Cs^+ atoms perform a head-to-head motion, which is the displacement of two neighboring Cs^+ atoms towards the same face, along the $\langle 100 \rangle$ directions.

Comparative studies of $MAPbX_3$ and $CsPbX_3$ demonstrated several correlating Raman peaks representing the analogous motions for both compounds [43, 132]. Despite the existence of molecular dynamics simulations performed for $FAPbI_3$ [16, 17], its vibrational behavior and internal dynamics have not been correlated with experimental data so far. Only one Raman peak at 110 cm^{-1} has been experimentally determined [45]. There is also no experimental data for the mixed FA-based compounds at all.

Raman spectra of hybrid perovskites are usually analyzed in three spectral ranges which correspond to different sources of vibrations[65]. **In this thesis, we named them Zone I, II, and III to increase readability.** The low-energy range (Zone I) contains PbX_6 sublattice modes. It extends from 10 to 50 cm^{-1} for iodides and to 60-65 for bromides. Zone II, or middle range frequencies, corresponds to the coupled modes that appear exclusively in LHPs. They represent the molecular reorientation of the organic cation and the influence of the PbX_6 octahedral framework. Zone III, the high-energy zone, includes individual molecular modes. It extends from 500 to 3500 cm^{-1} for FA^+ and from 800 to 3200 cm^{-1} for MA^+ . It is worth noticing that all modes are affected by coupling, however, this coupling is the source of the vibration only in Zone II. The modes of Zone I and III are present in isolated octahedra and isolated molecules, respectively.

In the following, the experimental and theoretical modes from literature are presented. It is important to remark that not all references detailed the mode positions. These were extracted from the graphics, which were converted to data using WebPlotDigitizer-3.8 and fitted in Peak-o-mat 1.2.9. Both software is open source. Tables 2.2 and 2.3 present the experimental and computational details of each publication, while Tables 2.4, 2.6 and 2.7 show the Raman modes of LHPs with MA^+ , FA^+ and Cs^+ cations in the A-positions, respectively.

It is clear from the tables, that $MAPbX_3$ compounds have been vastly studied. $FAPbX_3$ has only been detailed for high-frequency modes and the $CsPbX_3$ Raman spectrum is the less explored.

Table 2.2: Experimental work on Raman spectroscopy of LHPs. Samples are categorized as thin film (TF) or single crystal (SC).

Ref	Material	Sample	Synthesis	Laser (nm)	T (K)
[62]	$MAPbI_3$ $MAPbBr_3$	TF	Deposition one step spin-coated	785	RT
[86]	$MAPbI_3$ $MAPbBr_3$	TF	Deposition one step spin-coated	514, 785, 1064	RT-100
[65]	$MAPbI_3$ $MAPbBr_3$	SC	Inverse temperature crystallization in GBL	785, 633, 488	90-300
[132]	$MAPbBr_3$	SC	Diffusion of isopropyl alcohol vapor into a 1M solution	633	80,400,500
[43]	$MAPbBr_3$	SC	Diffusion of isopropyl alcohol vapor into a 1M solution	633	80-480
[63]	$MAPbI_3$ $MAPbBr_3$	SC	Inverse temperature crystallization in GBL/DMSO/DMF	785, 1064	RT
[131]	$MAPbI_3$ $MAPbBr_3$	SC	Inverse temperature crystallization in GBL/DMF	1030	RT
[124]	$MAPbBr_3$	SC	Inverse temperature crystallization in DMF	632	RT
[45]	$FAPbI_3$	SC	Inverse temperature crystallization in GBL	514	RT
[103]	$FAPbI_3$ $FAPbBr_3$	SC	antisolvent vapor-assisted crystallization	1064	RT
[123]	$FAPbBr_3$	SC	Purchased	671	RT
[138]	$CsPbI_3$	SC	inverse temperature crystallization in degassed $HI-H_3PO_2$	532	RT
[106]	$FAPbI_3$	SC	solid state reaction of CsI and PbI_2	532	RT
[132]	$CsPbBr_3$	SC	Bridgman method	633	80,400,500
[43]	$CsPbBr_3$	SC	Diffusion of isopropyl alcohol vapor into a 1M solution	633	80-480
[18]	$CsPbBr_3$	SC	Solution grown	633	RT

Table 2.3: Theoretical work on vibrational modes of LHPs

Ref	Material	Method	T (K)
[65]	$MAPbI_3$ $MAPbBr_3$	DFT phonon calculations	90-300
[132]	$CsPbBr_3$	Theory from first principles MD, based on DFT	80-500
[18]	FA^+	B3LYP density functional hybrid method	RT

Table 2.4: Raman modes of $MAPbI_3$ and $MAPbBr_3$. Super index * refers to calculated modes.

Mode description	$MAPbI_3$	$MAPbBr_3$
Octahedra Twist [65]	19,27,29[65]* 28,31[65]	39,47 [65]
Octahedra Distortion[65]	33, 35, 35[65]* 35[65]	58[65]
Nodding Donkey around N [65]	52[62]56[65]58[65]*	
Nodding Donkey around N [65], asym.bend X-Pb-X [86]	65[86] 66[65]*	66[65, 86]
Lurching MA[65]	69,75[65]* 73,78,81[65]	129[65]
Lurching MA[65], asym.bend X-Pb-X[86]		99[65, 86] , 134[86], 138[65]
Lurching MA[65], degradation grain boundaries[62]	92[65]* 94[62]95[65]	
Nodding Donkey around C[65], asym.stretch Pb-X[86]	103[86] 110[62]117[65]*	
Attempt roll around C-N[65]	128[65]*	
Nodding Donkey around C[65]	133[65]* 138[65]	
C-N torsion[65, 86] , degradation grain boundaries[62], MA rotation [124, 131]	220[62], 249[86], 275 [131], 315[65]*, 199,223,243,272,312[65]	297,326[65], 275 [131], 323[86], 325 [124]
Displacement of atoms in MA[65], rocking MA[86, 124, 131] , NH ₃ wagging [43]	876[65]* , 889[65], 909 [131]	915[65], 917[86], 913[43, 124], 921[63], 922 [131]
C-N asym.bend[65], rock MA[86]	909[65]*, 911[86], 916[65]	970[65]
C-N stretch[43, 63, 65, 86, 124]	956 [131], 960[86], 965 [124], 968[65],1007[65]*	968[86], 968[43], 970 [131], 978[63], 994[65] 1143,1178[65], 1161[63]
Stochastic disorder [65]		
C-N sym.bend[65]	1008[65]1215[65]*	
C-N sym.bend[65], rock MA [86, 124, 131]	1043[65], 1234[65]*, 1247[86], 1249[124], 1250 [131]	1236[65], 1248[86], 1249[131], 1257[63]
CH ₃ asym. Breath[65]	1378[65]*	1352[65],1362[63]
CH ₃ sym. Breath[65], CH ₃ sym.bend [86], NH ₃ sym. Bending [131]	1418,1425[65]*, 1420 [65], 1424[86], 1426[131]	1421[65], 1428[86], 1430 [131]
CH ₃ sym. Breath[65], CH ₃ asym.bend [86]		1445[63], 1450[86], 1458[65]
NH ₃ asym. Breath[65, 124], NH ₃ bend[86]	1444, 1469[86], 1457[65], 1464[65]*, 1469 [131], 1473 [124]	1478[86] , 1471[65], 1480[131]
NH ₃ sym. Breath[63, 65]	1542[65]*	1505[63] 1573[65]
NH ₃ sym.breath[65], NH ₃ asym.bend[86], NH ₃ twist [124, 131]	1558[65]*, 1580[86], 1586[65], 1583[131], 1590[124]	1587[86] 1590[65], 1593[131], 1610,1801[63]

Table 2.5: Continuation of Table 2.4

Mode description	$MAPbI_3$	$MAPbBr_3$
C-H asym.stretch[65, 124], combination of modes[86], $N^+ - H$ stretching [131]	2706,2821,2906[86], 2820 [124], 2949[65], 2957[124], 2971[65]*	2714,2827,2846[86], 2821[65], 2897,2913,2927[43], 2893 [131] 2893[131],
C-H sym.stretch[43, 63, 65, 124, 131], CH3 asym.stretch[86]	2949,2949[65], 2957[124], 2959[86], 3067,3074[65]*	2896, 2965[65], 2966[86], 2970[43], 2971[63]
N-H asym.stretch[65], N-H sym.stretch[86], $N^+ - H$ sym. Stretch [131]	2949[65] 3087[65]*	2832[131], 3031[43], 3033[65], 3035[86]
N-H sym.stretch[65, 86, 124, 131]	2949,2949[65]2993[86], 3024, 3113, 3169[124], 3096,3199[65]*	3044,3128, 3189[131], 3083,3121[43] 3106, 3144[65]

Table 2.6: Raman modes of $FAPbI_3$ and $FAPbBr_3$. Super index * refers to calculated modes, while + refers to experimental modes that were not identified or attributed in their respective publication.

Mode description	$FAPbI_3$	$FAPbBr_3$
Tilting and distortion of the octahedra [123]	111 [45]	70, 464+, 494+, 250[123]
$NH_2 - C - NH_2$ bending [60, 103, 123]	516[103]	520[103, 123] [60]*
NH_2 torsion [60, 103]	584 [103]	590 [103]
NH2 wagging [60]	701[103]	708 [103],708+ [123], 587,601[60]*
NH_2 torsion +C-H out-of-plane bending [60]		746+ [123], 718[60]*
NH_2 rocking [60]		1047[60]*
C-H in-plane bending+ NH_2 rocking [60]		1084[60]*
C-N sym.stretch[60, 103, 123] + NH_2 rocking [60]	1112[103]	1109[123] , 1111[103], 1130[60]*
C-H in-plane bending+ C-N stretch [60]	1342+[103]	1354+ [103], 1388[60]*
NH_2 rocking [60]	1380[103]	1389 [103], 1419[60]*
C-H in-plane bending[123]+ NH_2 sym. bending	1550 [103]	1555[103], 1558[123]
asym.[103] NH_2 in-plane bending[60, 123]	1613 [103]	1620[103], 1617,1643+ [123], 1645,1741[60]*
NH_2 in-plane bending +C-N stretch [60, 123]		1717[123], 1789[60]*
C-H stretch[60, 123]		3028,3088[123], 3208[60]*
NH_2 sym. stretch [60, 123]		3552, 3566 [60]*, 3241,3332[123]
NH_2 asym. stretch [60, 123]		3669, 3671 [60]* ,3413[123]

Table 2.7: Raman modes of $CsPbI_3$ and $CsPbBr_3$ presented in literature

Mode description	$CsPbI_3(\delta)$	$CsPbBr_3$
Tilting and distortion of the octahedra [43, 132], Cs^+ motion [106]	48, 55, 66 [138], 47, 56, 64 [106]	13,15,21,38,47, 49 [43], 28,65[132]
Halide motion [43], Halide and Cs^+ head-to-head motion [18, 106, 132]	97,108,117 [138], 84, 96, 107,115 [106]	72[43, 86]73[18] 79[132] 124[43] 128[18] 130[132] 144[132]
Halide motion [43] , second order phonon mode $PbBr_6$ [18]		310[18] 320[43]

2.1.6 $FAPbI_3$

As previously presented, $FAPbI_3$ is used as a photoactive material for thin-film solar cells. Its strengths lie in its narrow bandgap (1.5 eV) which is close to the Shockley-Queisser limit, high decomposition temperature (320°C) vs 275°C) [45, 72, 90] and easier solution processability compared to the inorganic $CsPbI_3$ [45, 90, 92, 140]. Its highest weakness for device implementation is the transformation into a degraded state, which is not photoactive. It can be visually perceived as the transition of a black crystal into yellow, as shown in Fig. 2.8.

**Figure 2.8:** Visual degradation of $FAPbI_3$ (different crystals)

The crystal is obtained from a γ -butyrolactone (GBL) solution at temperatures from 90°C to 120°C, remaining stable in the GBL solution at temperatures above 60°C [104, 112]. Then, it degrades due to internal strain [141]. This transition takes place in less than 1 day if single crystals are stored in ambient air with a humidity rate of 55-57% and up to 10 days when they are stored in vacuum or inert gas [45, 104]. A photoactive polycrystal can be thermally recovered from the degraded crystal by placing it at a high temperature for some minutes. This method varies between 140°C to 180°C and 2 to 15 min. According to differential scanning calorimetry, this reverse transition presents an endothermic peak at 160°C for powder and 185°C for single crystals [45, 49]. The degradation of this polycrystal does not take place until 20 to 30 days [9, 37, 69, 112, 129]. Chemical decomposition of single crystals occurs at higher temperatures: HI decomposes around 320°C-360°C, while FA^+ around 375°C-420°C [45].

Hence, we recognized here three states: as-synthesized, degraded, and thermally recovered. The as-synthesized and the thermally recovered are both photoactive and there are known in the literature as the α -phase, while the degraded state is known as the δ -phase.

The structure of the δ -phase is accepted as hexagonal $P6_3mc$ [112]. The lattice constants are $a = 8.660$ and $c = 7.9022$. As seen in Fig. 2.9a, two cations are surrounded by the inorganic frame. This frame is composed by four inorganic 2-fold octahedra (Fig. 2.9b).

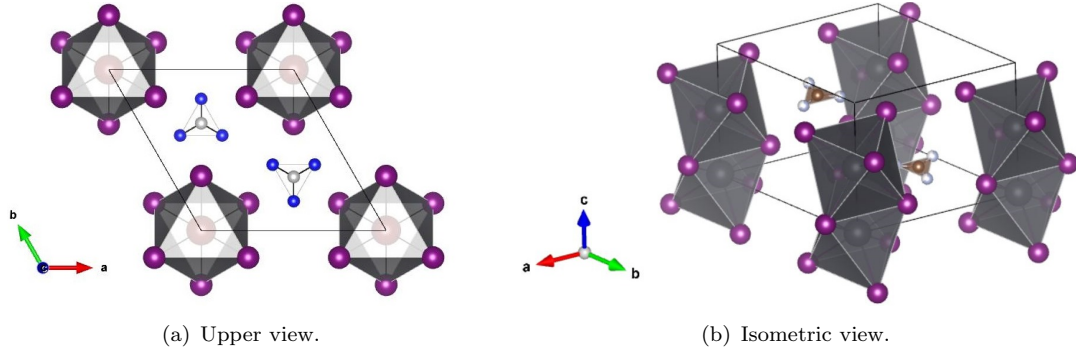


Figure 2.9: Representation of δ -phase. The orthogonal axes are shown at left of each figure. Red spheres represent Pb, purple are I, white C and blue N. For simplicity, H atoms are not represented. The FA^+ molecule is schemed simultaneously in its three possible positions.

On the contrary, there is no consensus about the structure of the α -phase. In 2013, Stoumpos et al. defined the α -phase as trigonal $P3$ derived from single-crystal X-Ray Diffraction (XRD) studies [112]. In 2015, Weller et al. carried out XRD and powder neutron diffraction on the thermally recovered $FAPbI_3$ and attributed cubic $Pm\bar{3}m$ symmetry [129]. In literature, as trigonal as cubic structures are attributed to $\alpha - FAPbI_3$. However, some publications propose different structures or simply use "quasi-cubic" to simplify the material distortion. Moreover, a myriad of material characteristics is explained as a consequence of the chosen structure. Examples are listed in the following. The discussion arises when the structural instability of the α -phase and the structure of the molecular cation are considered. First, Goldschmidt's tolerance factor of $FAPbI_3$ is equal to 1.008, which predicts structural stability for perovskites. If the structure is ideal cubic as predicted by this factor, it should not present instability. Also, the combination with the cubic $Pm\bar{3}m$ $FAPbBr_3$ presents an instability region from 30 to 50% of $FAPbBr_3$, which was justified by the difference of space group when the α -phase is considered as trigonal [77]. Bandgap calculations obtained by Density Functional Theory (DFT) exhibit an energy 0.2 eV lower than the experimentally observed with a cubic $Pm\bar{3}m$ model [4]. A more precise result (+0.05 eV) results from a relaxed tetragonal structure with head-to-tail cation organization. In this organization, the mean axis of FA^+ , N-N, is perpendicular to the adjacent molecules. Molecular dynamics simulations and group theory calculations show octahedral distortions in $FAPbI_3$ at 27°C, responding to a cubic symmetry $Im\bar{3}$. In this case, the body-centered cell is eight times larger than the primitive one [16, 17]. Additionally, at 93°C harmonicity of the vibrations stabilize the structure as the cubic $Pm\bar{3}m$.

Even though there is an agreement in $FAPbI_3$ distortion, there are no deterministic experiments. One reason is that molecular dynamics are usually dismissed in bulk average results. Additionally, the as-synthesized and the thermally recovered states are not often differentiated, albeit there is a considerable difference in the structural stability.

2.2 Optoelectronics

The first approach of hybrid halide perovskites for optoelectronic applications was made by Mitzi in 1994 [82]. It was focused on solution-processable transistors and LEDs using hybrid tin halide layered (2D) perovskites. However, the first application of 3D hybrid lead halide perovskite as the thin film was made in 2009, where $MAPbI_3$ and $MAPbBr_3$ were used as the photo-active material in a solar cell. The device with $MAPbI_3$ showed an efficiency of 3.8% and very poor stability [56].

Nowadays, perovskites are used in myriad optoelectronic applications [21], such as light emitting devices (LEDs) [139], solar cells [56, 77, 136], photo-transistors [67, 126], lasers [125, 142], and detectors [25, 85, 127, 133]. Depending of the desired proprieties, the nanostructure dimension varies from 0D quantum dots, passing thought 1D nanowires/nanorods and 2D quantum wells/nanoplates, to 3D single crystalline and polycrystalline thin films. This is a result of the properties of engineering such as morphology, structural characteristics (size, shape, thickness), compactness, defectiveness, and crystallographic orientation. Among these properties are: sharp absorption edge, high absorption coefficients, the large diffusion length of free charge carriers, low recombination rates [112], bandgap tunability [27, 77, 87, 113, 135], the small difference between the bandgap size and the open circuit voltage [110], easy processing, and high defect tolerance [83, 143].

Albeit the dimensionality of the perovskite structure depends on the target application, this thesis is focused on **3D thin films** since they are the most investigated and promise the best efficiency. For this reason, only the application where this structure suits better will be analyzed. Among them, the most prominent application is the solar cell, with several research centers in the world specializing in the efficiency enhancement of this technology. Other applications with outstanding results are photodetectors, radiation detectors, and LEDs, where perovskite implementation achieves high responsivities, high detectivities, and high external quantum efficiency and brightness, respectively.

A brief description of the application of perovskites in a few optoelectronic devices and their performance is given below [21].

- **Solar cells** converts incident light into an electrical current through the photovoltaic effect. Hybrid perovskites are applied normally in form of polycrystalline thin films in p-i-n or n-i-p structures. The currently certified record efficiency for single-junction perovskite solar cell is 25.2% using $FAPbI_3$ [50], which competes with established Si-technologies. Polycrystalline thin films are more used than single crystalline films due to the high defect tolerance
- **Photodetectors** capture the incident light and convert it to electrical signals through the photoelectric effect. The interesting properties of halide perovskites for this application are direct and widely tunable bandgap, high absorption coefficient, and high charge-carrier mobilities. For $MAPbI_3$ thin films, the responsivity and detectivity reach around 20 AW^{-1} and $10^{13} \text{ cmHz}^{1/2}\text{W}^{-1}$, respectively. It also presents low noise levels in the order of $2 \text{ fAHz}^{-1/2}$. Single crystal thin films are the best fitting due to the lack of grain boundaries which gives them low trap density and high

charge carrier mobility. Films of $MAPbBr_3$ and $MAPbI_3$ have been used in the vertical p-i-n structure.

- **Light emitting devices (LEDs)** emit light when current flows through it. The best-suited structures of perovskite for this application are nanowires or nanorods due to the high light extraction, large active surface area, and directional charge carrier transport that leads to high carrier injection efficiency. When films are involved, lesser crystallinity is beneficial in order to exhibit more defect-induced radiative recombination centers for light emission. In parameters, the electroluminescence wavelength varies from 410 up to 780 nm and the external quantum efficiency reached 9%. The record luminance for perovskites reaches 12000 cd m^{-2} .

Even though a great improvement has been achieved for perovskite optoelectronics, there are still challenges to their performance and subsequently, commercialization. Among these are toxicology, stability issues[141], UV and moisture degradation, hysteresis, ionic migration, photocurrent loss, and carrier shunting. The solution deposition of thin films generated non-uniform layers with pinholes that affect the device's performance. Strong efforts are made worldwide to provide highly oriented polycrystalline films and single-crystal thin films.

Focusing on the stability problem, the proposed solutions in the literature are compositional engineering, oriented growth via additives,. The first solution includes the combination of different cations on the A-site or halides on the X-site. The atomic substitution strongly impacts the performance. For example, in the quinary $Cs_xFA_{1-x}Pb(I_{1-y}Br_y)_3$ composition, x, and y should be maintained at about 10 % each. This strategy has been shown to improve phase stability in bulk, microcrystalline and nanocrystalline forms. In solar cells, this is translated into improved photo-and moisture stability in environmental conditions and reduction of trap density, which consequently increases the efficiency by more than 1%[33, 68, 70, 77, 85, 136] It is also accompanied by band gap tunability.

Chapter 3

Experimental details

To understand the effect of composition on the atomic dispositions, Raman spectroscopy was chosen since it reveals the vibrational spectrum, providing information about chemical structure, structural phases, degree of crystallinity (defectiveness), and molecular interactions, among others. Complementary experiments such as X-Ray diffraction (XRD) and Photoluminescence (PL) measurements were performed to support analyses, providing further information.

For the Raman experiments, the measurements were conducted on single crystal (SC) perovskites which exhibit fewer defects compared to their polycrystalline counterparts. Solution-based growth provides an even distribution of components and a good level of process control. PL as a side-measurement of Raman spectroscopy was also performed onto SCs. Additionally to SCs, XRD could be measured on powder and thin films.

3.1 Sample preparation

In this thesis, the perovskites studied were:

- $MAPbBr_3$, $MAPbI_3$
- $CsPbBr_3$
- $FAPbBr_3$, $FAPbI_3$
- $Cs_{0.1}FA_{0.9}PbI_3$, $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$

Additionally, temperature-dependent Raman spectroscopy was done on FAI and MAI salts.

The SCs, except $FAPbI_3$, were synthesized by the ETH- Zurich Group: O. Nazarenko, D. Dirin, and M. Kovalenko. For reproducibility, the author synthesized the iodide compounds, which are faster to deteriorate from their initial state than bromide compounds. The synthesis and treatment of $FAPbI_3$ SCs were solely performed by the author.

Thin films were deposited by S.H.B.V Kumar from the Group "Technologies for thin-film devices" at the Technical University Berlin.

3.1.1 Single crystals

Single crystalline samples of the perovskites were prepared using the modified inverse temperature crystallization (ITC) method reported elsewhere [24, 45, 85, 104]. The precursors employed were FAI, FABr, MAI, MABr, CsBr, PbI_2 and $PbBr_2$.

For iodide-containing compounds, 1 M of the salt precursor and the lead halide were dissolved in 1 ml of GBL at room temperature in a controlled N_2 atmosphere ($H_2O < 1 ppm$, $O_2 < 10 ppm$). Solubility was increased by placing the vials over a preheated hot plate at 60°C for at least 1 h. The solution was then filtered through the 0.2 μm polytetrafluoroethylene syringe filter, poured into a 10 ml vial, and placed over a preheated hot plate, arranged so that only the bottom was heated. To ensure the nucleation of a seed, the vial was in contact with a metal piece, previously placed on the hot plate. The starting temperature of the hot plate determines the size and quantity of the crystals, as seen in Fig. 3.1. Leaving the solution at 120°C for 3 hours creates several single crystals of ca. 0.5 mm, useful for XRD measurements. For larger crystals of ca. 1 cm, the solution was placed at 90°C, elevated stepwise at 5°C/h up to 120°C. The maximum temperature was kept for 3 h to increase the crystal size. To grow large enough crystals of the $Cs_{0.1}FA_{0.9}PbI_3$ and $FAPbI_3$ compositions, a previously obtained seed was introduced at 90°C into the solution and kept for 3 more hours.

ETH- Zurich Group SCs synthesis differs from the author's in the set-up for heating. They poured the filtered precursor solution of 3 ml volume into a 20 ml vial, closed with a cap, and placed it into a preheated (90°C) glycerol bath. For $FAPbBr_3$ and $MAPbBr_3$, the synthesis process was analogous except for the temperature range (from 60 to 80°C) and solvent (DMF=N, N-dimethylformamide). Independently of the growth method, the resulting crystals were wiped with a filter paper and dried with N_2 gas flux.

Some photos of the single crystals are shown in Fig. 3.2.

Powder samples were obtained by grinding single crystals in an agate mortar.

3.1.2 Thin films

Thin films of $FAPbI_3$ were prepared by a modified method of the two-step spin-coating deposition proposed by Han et al.[45]. 450 mg of PbI_2 was dissolved in 1 mL dimethylformamide and the solution was placed over a preheated hot plate at 60°C for at least 1 h. FAI was dissolved in 2-propanol and left at RT for the same time. The PbI_2 solution was spin-coated over glass substrates at 2500 rpm for 30 s and left at 70°C for 10 min. Then, FAI was spin-coated on top at 3000 rpm for 30 s in the dry air. Samples were annealed at different temperatures: 80°C, 100°C, and 120°C for 45 min. All operations were performed inside the glovebox. These temperatures were chosen to disclose a difference, if exists, to the single crystals which form and grow in a temperature range 90°C-115°C.

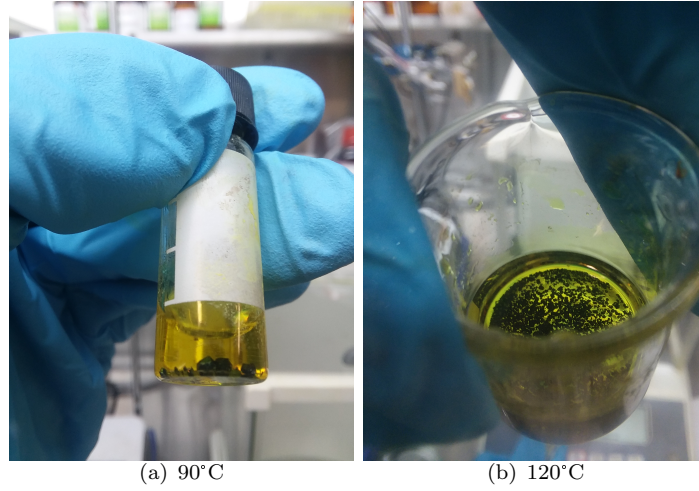


Figure 3.1: $FAPbI_3$ crystal size dependence on the starting synthesis temperature.

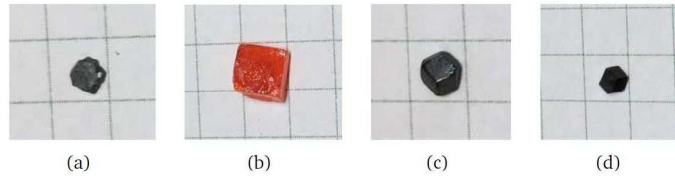


Figure 3.2: Photographies of single crystals: a) $FAPbI_3$, b) $FAPbBr_3$, c) $Cs_{0.1}FA_{0.9}PbI_3$ and d) $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$

3.2 Characterization Techniques

The author used Raman spectroscopy and PL to characterize the samples. Due to the strong support that additional information gave to the analysis, XRD, measurements were externalized. XRD was performed by Ruslan Muydinov, Technische Universität Berlin and Olga Nazarenko, ETH Zürich. It is worth noticing that the post-processing of the data, such as the fitting and noise clearing, the interpretation, and analysis was performed by the author.

As clarification: room temperature is defined as a range from 15°C to 30°C, wherein the studied materials do not present phase transition.

3.2.1 Raman spectroscopy and PL

Raman spectroscopy was performed on a high-resolution LabRAM HR800 spectrometer from Horiba. The ultra-low frequency (ULF) unit allowed to extend the frequency range from 10cm^{-1} for the excitation wavelength of 633 nm. The laser beam was focused using 50x/0.75 and 100x/0.90 microscope objectives and a power intensity in a range from $6\mu\text{W}$ to $280\mu\text{W}$. Spectra were recorded with gratings of 600 and 1800 lines per millimeter at RT in the ambient environment because air does not affect the measurements [31]. The reproducibility of the measurements was probed through the analysis of several samples. An example of this is shown for $FAPbI_3$ polymorphs, whose normalized Raman spectra

are present in Fig. 3.3. The position of the Raman modes does not vary, supporting our attribution. The difference in intensity is related to the instrument adjustment or the measurement point.

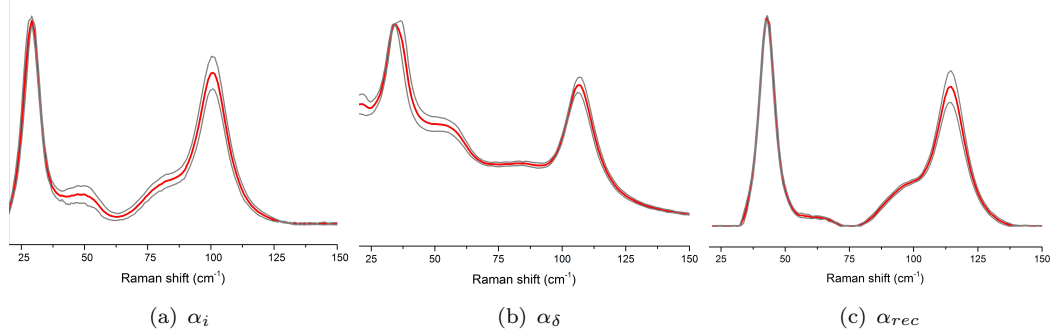


Figure 3.3: Average Raman spectra of different samples and standard deviation. The average value ($\bar{x}$) are presented by the red lines, while the standard deviation of each point (σ) are presented by the grey line ($\bar{x} + \sigma, \bar{x} - \sigma$).

We notice here that the acquisition and interpretation of Raman spectra are challenging in the case of the LHPs, due to the combination of two counteracting effects: (i) the low relative intensity of Raman scattering compared to the primary excitation power and (ii) the high rate of degradation of LHPs under laser-induced heating[62]. For a laser wavelength of $\lambda=532$ nm, the LHPs are degraded under a beam power higher than $> 10\mu W$. We detected degradation of FA-based LHPs into PbI_2 under $> 1mW$ under an excitation wavelength of $\lambda=633$ nm, as appreciated for $FAPbI_3$ in Fig. 3.4.

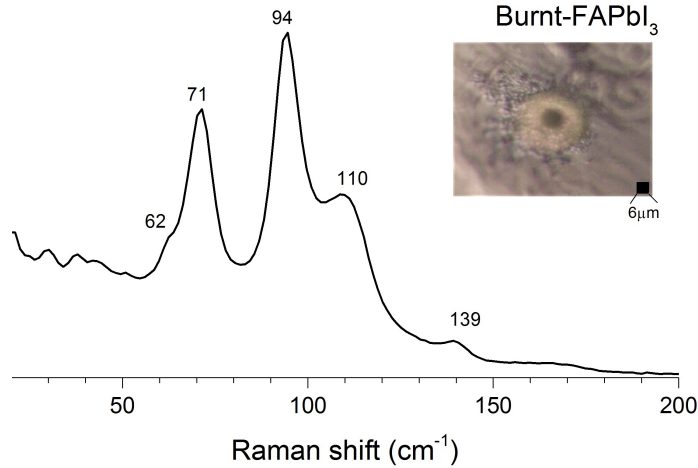


Figure 3.4: Raman spectrum of PbI_2 resulting from placing $FAPbI_3$ under an excitation power higher than 1 mW ($\lambda=633$ nm).

Consequently, the excitation power and integration times were optimized for each LHP to ensure a good signal-to-noise ratio while avoiding laser-induced material degradation during the measurements. To avoid parasitic light signals, the measurements were performed in darkness. Due to the onset of strong luminescence in $FAPbI_3$ (PL signal around $\lambda=827$ nm), the Raman spectrum of this compound is only shown until 200 cm^{-1} . The same

limitation applies to mixed compounds at frequencies above 1200 cm^{-1} . For CsPbBr_3 , the spectra were found to be informative up to 400 cm^{-1} .

Despite the limitation in the measured range, the source at $\lambda = 633\text{ nm}$ gives the sharpest peaks and lowest noise. A less energetic excitation source ($\lambda = 830\text{ nm}$) also excites FAPbI_3 , emitting PL that reduces the possibility of identifiable peaks.

For MAI and FAI, the spectra were recorded with a mesh of 600 lines/mm under an excitation wavelength of 820 nm at $450\text{ }\mu\text{W}$ at RT in the ambient environment. Due to hardware restrictions, the Raman spectra were measured until 1800 cm^{-1} .

Temperature-dependent Raman spectroscopy measurements were performed in module THMS600 from Linkam Scientific. For heating, the chamber of the module was open during measurements to avoid water condensation over the sample. FAPbI_3 was heated from 20 to 200°C and measured in temperature steps of 30°C , maintaining the selected temperature for 10 min for the sample to reach thermal equilibrium with the heating stage. After identifying a transition between 80°C and 110°C , additional measurements were done at 90°C , 95°C , and 100°C . PL measurements were performed in the same way, with temperature steps of 10°C and an integration time of 1 s. For cooling, the chamber of the module was kept closed and the temperature was decreased using liquid N_2 . The temperature varied between 25°C to -200°C , with a step of 25°C ($\pm 5^\circ\text{C}$).

For the study of FAPbI_3 polymorphism, we measured the as-synthesized SCs immediately after they crystallize and are wiped. The SCs remain in the as-synthesized state for less than 24h in air, degrading heterogeneously. Within this time, the appearance of the FAPbI_3 samples became yellow at the eye. After 24 h of air exposition, the spectra of the degraded samples were obtained by micro-Raman maps with a spacing of $5\text{ }\mu\text{m}$ to scope the heterogeneous surface. The recovered samples were obtained by heating the degraded samples to 180°C for 2 min on a hot plate and cooling down to RT [45]. The recovered samples were measured immediately after preparation. The preferable sample positions to measure the samples as-synthesized were located at the crystal borders or side planes, where the PL signal is lowered enough to disclose the low-frequency zone ($<200\text{ cm}^{-1}$).

3.2.2 XRD

Powder XRD patterns, obtained by *Olga Nazarenko at ETH Zürich*, were collected in transmission (Debye-Scherrer-Geometry) with STADI P diffractometer (STOE & Cie GmbH), equipped with a silicon strip MYTHEN 1K Detector (DECTRIS) with a curved Ge (111)-Monochromator. For the measurement, single crystals were ground and placed between adhesive tapes. This measurement was used in *Chapter 4.3*.

Thin film, powder and single crystal (ca. 0.5 mm) XRD were performed in ambient air by *Ruslan Muydinov at the Technische Universität Berlin*. The patterns were acquired using Cu Ka radiation on a D8 Discover diffractometer from Bruker. A high-resolution model of the LYNXEYE XE-T detector in combination with the 2.5° axial parallel-slit collimators and 0.6 mm slits from primary and secondary beam sides was used. Measurements were performed in a Bragg-Brentano geometry with 0.02° step size and 2s step time. These

measurements were done immediately after the preparation of the samples to avoid any visible $\alpha \rightarrow \delta$ phase transition. The fastest transition was visually observed for the as-prepared $FAPbI_3$ films crystallized at 80°C and took 2 hours, but even in this case, the XRD experiment proceeded faster. Temperature-dependent XRD measurements were conducted in ambient air as described above using the high-temperature chamber TC-DOME with Be-walls from Anton Paar. XRD patterns were recorded for several selected temperatures in the range from 30°C to 180°C. Each pattern ranged from a 2θ range of 5° to 70° with a step size of 0.01° and an integration time of 1.2 s per step. These measurements were used in *Chapter 5.1*

XRD patterns were fitted in the *software* TOPAS program using the Pawley method, which use the indexed peak positions and the lattice symmetry to refine peak intensities. Weighting of partial phases = (Abs(Yobs-Ycalc) / Abs(Yobs+Ycalc) +1) / Sin(X Deg / 2);

3.3 Computational details

3.3.1 DFT calculations

DFT calculations were performed by *Hossein Mirhosseini and Manjusha Chugh at the Technische Universität Paderborn.*

FAPbI₃ and *FAPbBr₃*: DFT-based total energy and force calculations were performed using the Vienna Ab initio Simulation Package (VASP) code [10]. The projector augmented (PAW) potentials [58, 59] that describe electron-ion interactions were constructed such that the 5*d* electrons of Pb, 4*s*, 4*p* electrons of Br, and 5*s*, 5*p* electrons of I are treated as valence electrons. The plane-wave cut-off energy was set to 700 eV. A force convergence criteria of 1 meV/Å and an energy convergence of 10⁻⁶ eV were used for all geometry optimizations. A Γ -centered Monkhorst-Pack set of k-points of 6x6x6 was used for Brillouin zone integration. To take the weak Van der Waals interactions into account, the optB88-vdW functional [55] with a default setting of the VASP was used. Cubic phases of *FAPbI₃* and *FAPbBr₃* perovskite compounds with experimentally measured lattice parameters (6.36 and 5.99 Å, respectively) were considered. Spin-polarized calculations for the primitive cells and 2x2x2 cells showed no change in the atomic configuration, therefore, the rest of the calculations were performed on primitive cells. First-principles lattice dynamics (phonon spectrum) calculations were performed for the cubic phases of *FAPbI₃* and *FAPbBr₃* by diagonalizing the Hessian matrix within the Harmonic approximation [32]. We used the finite difference method to calculate the force constants. The eigenvectors of the Hessian matrix give the normal modes of the vibrations of the atoms, whereas the eigenvalues represent their frequencies. After obtaining the normal modes, Raman intensities (activities) of these modes were obtained by calculating the change in polarizability (macroscopic dielectric tensor) of each normal mode. Diagonalization of the Hessian matrix gives imaginary frequencies if the structure is not well optimized. Hence, we first optimized the atomic structures with rather tight convergence criteria as mentioned above.

FA^+ and MA^+ : The first step in the theoretical calculation of vibrational spectra is to calculate the vibrational normal modes of a molecule. For isolated molecules in the gas phase, usually static calculations based on harmonic approximation are sufficient. Using the CP2K program [61], we simulated isolated molecular cations of MA^+ and FA^+ by placing each of them in a cubic box of side length 16 Å. Their molecular structures were optimized using a tight force convergence criteria of 5.0×10^{-5} hartree/Bohr. The exchange and correlation functional used were Becke97 [8]. The DFTD3 van der Waals dispersion correction of Grimme was also included [42]. Polarized double zeta basis sets were used for each element in the cation. Eigenvectors of the Hessian matrix give normal modes of vibration whereas its eigenvalues give the frequencies of molecular vibration. The intensities of the IR and Raman spectra were obtained by calculating the change in dipole moments and polarizabilities, respectively, along the normal mode vectors using the finite-difference approach. The normal mode analysis is performed at 0 K temperature. To include anharmonicity effects, we calculated IR and Raman spectra of the isolated molecules from ab-initio molecular dynamics (AIMD) simulations. Using the above-mentioned exchange-correlation functional and basis sets, we obtained a 30 ps AIMD trajectory. The temperature of the thermostat was set at 300 K. From the coordinate trajectories of the cations, volumetric electron densities were obtained using the REFTRAJ ensemble approach in CP2K. To compute the electromagnetic properties (and IR and Raman spectra) of the cations from the obtained volumetric electron densities, we used Trajectory Analyzer and Visualizer (TRAVIS) software tool [12, 13, 119]. It utilizes the Voronoi integration scheme [120] to calculate the derivatives of dipole moments and polarizabilities.

These calculations were used in *Chapters 4.1 and 6.1*.

Chapter 4

Results

This chapter is divided into five parts:

1. Attribution of Raman modes
2. Zone I and II: Octahedral and pervoskite modes
3. Zone III: Molecular modes
4. Stability of mixed compounds
5. Application in thin-film optoelectronic devices

As mentioned in the Chapters above, this research focuses on the characterization of $FAPbI_3$ by Raman spectroscopy. The first section presents the calculation of theoretical Raman modes, necessary to perform an adequate analysis of the spectra. The following three sections are the interpretation of the experimental spectra of single crystals of pure $FAPbI_3$, divided in frequency zones, and of mixed compounds. The last section is the bridge toward application: The dependence of the deposition temperature of thin films on the material properties and how that affects the device performance.

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4.1 Attribution of Raman modes

In this chapter, we attribute the Raman modes of $FAPbI_3$, which have not been investigated in literature by calculations nor experimentally. An exception is the high-frequency zone ($> 500 \text{ cm}^{-1}$), which has been explored [103] and attributed according to the Raman modes of the isolated molecule [60].

Chapter 2.1 explains the results from DFT calculations of Raman modes $FAPbI_3$ and Chapter 2.2 presents the attribution of the experimental spectrum based on the previous results and a comparative analysis with $MAPbI_3$. Finally, the Raman modes are summarized in Chapter 2.3.

4.1.1 Theoretical Raman spectrum

DFT calculations are suitable to attribute Raman modes of LHPs. However, in literature only the Raman modes $MAPbI_3$ are calculated. Furthermore, they are corroborated experimentally by several authors [39, 65, 86, 131]. We developed our DFT model and proved it by calculating the $MAPbI_3$ Raman modes, which were in good agreement with literature data [65]. The calculated Raman spectra of $MAPbI_3$ and $FAPbI_3$ are shown in Fig. 4.1. We show only the Raman spectrum of $MAPbI_3$ until 310 cm^{-1} due to the absence of peaks below 800 cm^{-1} .

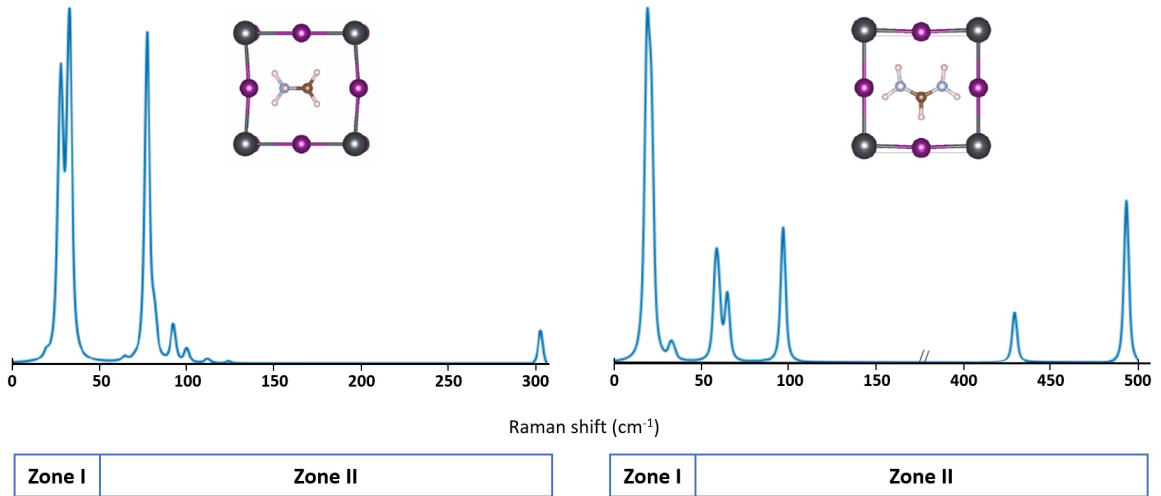


Figure 4.1: DFT calculated Raman spectrum for the cubic perovskites. left: $MAPbI_3$, right: $FAPbI_3$.

Zone I presents the octahedra modes, twist and distortion, proper of the O_h symmetry [65]. The twist mode is present at 16, 20 and 22 cm^{-1} and the distortion mode, at 33 and 35 cm^{-1} . As presented in Fig. 4.2, the octahedral vibration causes a relatively short displacement of the molecule compared to the cell size, which is shown by the red structures. This is a consequence of the lower mass of the molecule, $FA^+ = 46u.$, compared to the inorganic frame, $PbI_6 = 968u.$ Considering that the atomic mass of MA^+ is in the same order of magnitude, $28u.$, the Raman modes of $MAPbI_3$ should be located at similar frequencies

to $FAPbI_3$ in Zone I. Indeed, as shown in Fig. 4.1, $MAPbI_3$ presents the octahedral twist below 30 cm^{-1} , whereas the octahedral distortion peak appears between 30 and 50 cm^{-1} .

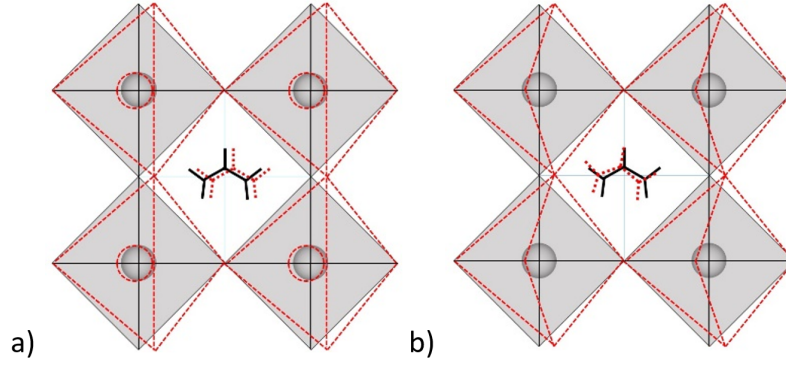


Figure 4.2: Octahedral modes of Zone I: a) twist and b) distortion.

Zone II of $FAPbI_3$ shows mainly six modes which are described at following. DFT calculations provide 3D models of the Raman modes, where displacements are represented by arrows. For simplicity, a 2D representation of the LHP modes is shown in Fig. 4.3, where the movement is represented by red lines.

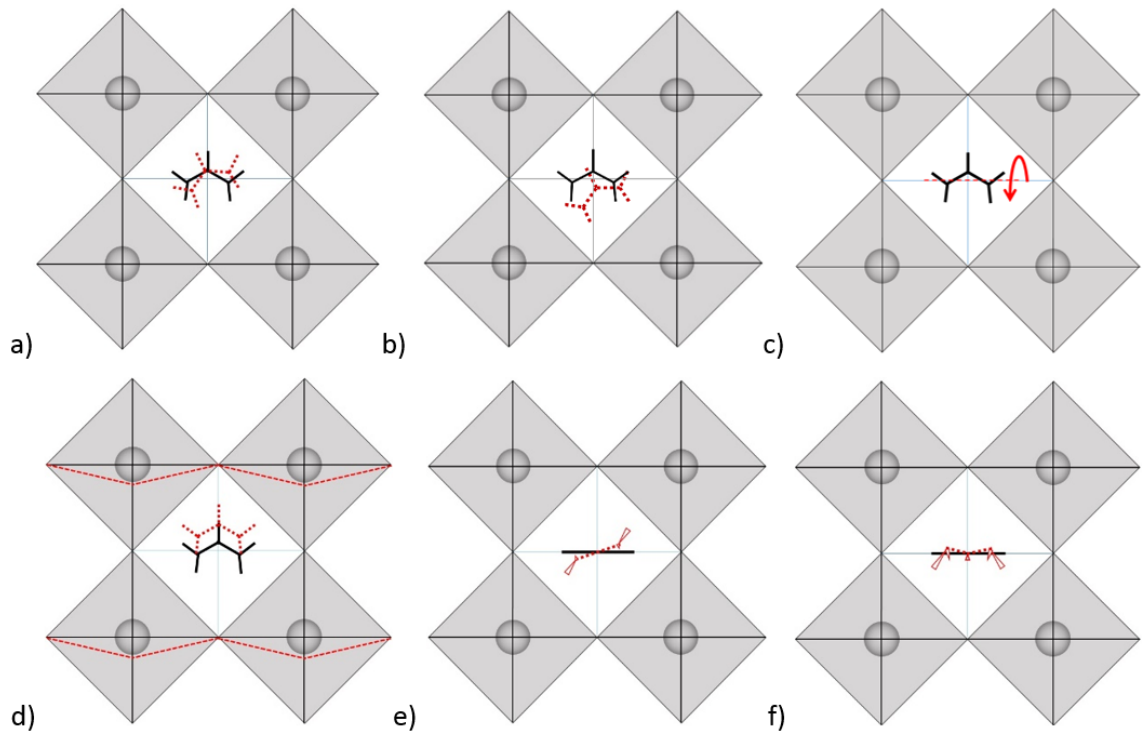


Figure 4.3: Schematic representation of the HP modes existing in $FAPbI_3$ according to our DFT calculations: a) in-plane rotation around center of mass, b) in-plane rotation around corner hydrogen, c) out-of-plane rotation around N-N axis, d) FA^+ translation along C-H bond, e) $H_2N - C - NH_2$ asymmetric out-of-plane bending and f) $H_2N - C - NH_2$ symmetric out-of-plane bending. Red colors represent changed positions. In cases e) and f) the N-H and C-H bonds project beyond the figure plane that is shown in the perspective view (thicker-closer).

- (a) in-plane rotation around the center of mass at 60cm^{-1} .
- (b) in-plane rotation around corner hydrogen at 61cm^{-1} .
- (c) out-of-plane rotation around N-N axis at 63cm^{-1} .
- (d) molecular translation at 97cm^{-1} .
- (e) asymmetric out-of-plane bending of $\text{H}_2\text{N} - \text{C} - \text{NH}_2$ at 429 cm^{-1} .
- (f) symmetric out-of-plane bending of $\text{H}_2\text{N} - \text{C} - \text{NH}_2$ at 494cm^{-1} .

4.1.2 Attribution of experimental modes

For the attribution of experimental modes, we compared the Raman spectrum of the as-synthesized FAPbI_3 to the DFT calculations, as presented in Fig. 4.4a. Due to the onset of strong luminescence around 820 nm, [45, 112, 129], the Raman spectrum could only be obtained until 200 cm^{-1} with a laser wavelength of 633 nm.

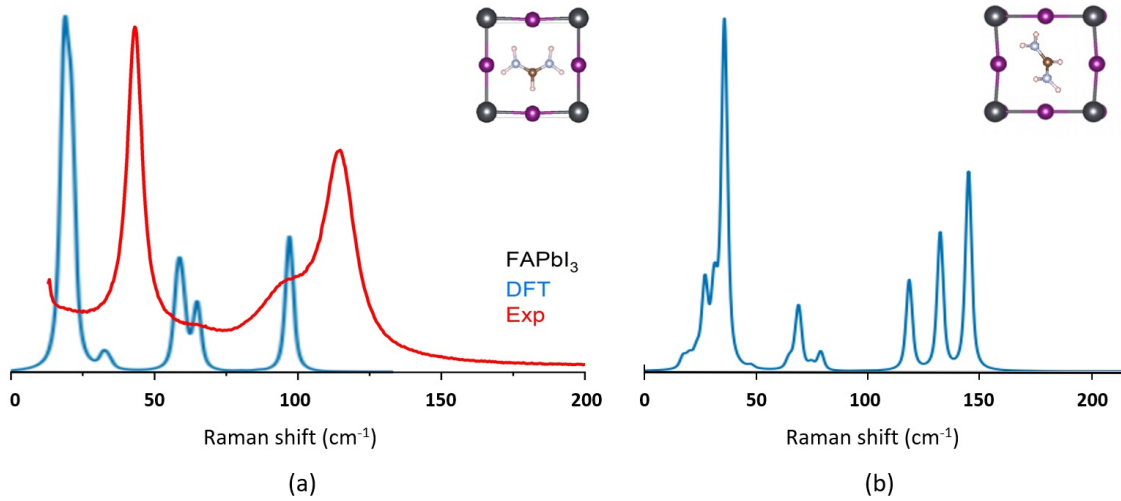


Figure 4.4: a) Comparison of the calculated (DFT, blue) and experimental (Exp, red) Raman spectra of FAPbI_3 and b) Calculated Raman spectrum of relaxed structure.

In **Zone I** of the experimental spectrum, the distortion mode is represented by a single peak at 43 cm^{-1} . The absence of splitting peaks indicated a cubic structure. Consequentially, this indicates a low displacement of Pb atoms in reality, as measured by neutron powder diffraction [129]. The absence of a twist peak could be attributed either to an unnoticeable intensity or mode inactivation.

In **Zone II**, the spectrum of FAPbI_3 shows a sharp peak at 114 cm^{-1} and two broad peaks at 63 cm^{-1} and 96 cm^{-1} . Compared to the calculated spectrum, the experimental peaks are blue-shifted. Such a difference may be caused by an experimentally weaker interaction between the FA^+ cations and the octahedra, the neglect of spin-orbit-coupling interactions, or a non-uniform disposition of FA^+ [4, 100, 112]. To evaluate the effect of the cation disposition in the unit cell, we performed DFT calculations of a relaxed structure with a rotated cation. The spectrum presented in Fig. 4.4b shows a myriad peak splitting,

indicating a high impact in the surrounding octahedra. As this pattern does not represent the experimental spectrum, a head-to-tail ordering is proposed. This organization is a low energetic arrangement of the molecules in which the $N-N$ axis of one FA^+ is perpendicular to the same axis of the adjacent molecules [4].

To validate the attribution of the experimental modes of $FAPbI_3$ to the mode description given by the DFT calculations, we compare the coupled modes for $FAPbI_3$ and $MAPbI_3$ [65]. It is worth noticing that significant differences exist between MA^+ and FA^+ , which are detailed in Chapter 2.1.3. Particularly, we remark the much lower dipole moment of FA^+ compared to MA^+ (0.21D vs 2.29D [34]) and the dimensionality of the molecule. While MA^+ presents a 3D C_{3V} symmetry, FA^+ is contained in a plane, with a C_{2V} symmetry. Therefore, the associated Raman modes may present higher frequencies compared to analogous modes of $MAPbX_3$. Taking into account these differences, corresponding coupled modes are compared.

- **Wagging rotation.** In $MAPbI_3$, its C_{3V} symmetry favour rotation in a cone vibrations. These modes can be either around N (58, 66 cm^{-1}), with a period of 0.3 ps [6], or around C (117, 133 cm^{-1}). In $FAPbI_3$, the C_{2V} symmetry and the rigid frame contain the wagging rotation in the molecular plane, around the corner H or mass center. Considering the low charge displacement in these FA^+ rotations, the analogy can be made with the rotation around N of $MAPbI_3$. In this sense, the calculated frequencies of $FAPbI_3$ (60, 61 cm^{-1}) are close to the experimental ones of $MAPbI_3$, allowing us to attribute the peak at 63 cm^{-1} to these modes. Furthermore, the experimental peak is broad, likely the superposition of both kinds of rotation.
- **Rotation around the main axis.** In $MAPbI_3$, the rotation occurs around C-N at 128 cm^{-1} . In $FAPbI_3$, the main axis is N-N, remaining the C-H bonds parallel to the {100} plane. The larger size, rigidity, and twist of a dipole moment stipulate slower rotation of FA^+ around the N-N axis. Indeed, this molecular movement presents a time constant of 2 ps, one order the magnitude larger than $MAPbI_3$ [6, 129]. Applying this consideration in the attribution, the calculated mode at 63 cm^{-1} is attributed to the experimental peak at 96 cm^{-1} .
- **Molecular translation.** In $MAPbI_3$, the molecular translation mode is split in several peaks at 69, 75, 81 and 92 cm^{-1} . In this vibration, the octahedra respond symmetrically to each other, combining twist and distortion modes. In comparison, $FAPbI_3$ octahedra present a distortion in one direction, as shown in Fig. 4.3d. Therefore, translation modes are expected at higher frequencies as compared to $FAPbI_3$ due to the weaker $PX_6 \leftrightarrow FA^+$ interaction. Consequently, we can attribute the calculated translation mode at 97 cm^{-1} to the peak at 114 cm^{-1} .
- **Torsion.** In $FAPbI_3$, the torsion mode proper of $MAPbI_3$ (315 cm^{-1}) is not expected due to the rigid N-C-N frame.

4.1.3 Summary

We attributed the Raman modes of the experimental spectrum of the as-synthesized $FAPbI_3$ for frequencies below 200 cm^{-1} .

The active modes are:

D Octahedral Distortion at 43 cm^{-1} .

M1 Molecular in-plane rotation at 63 cm^{-1} .

M2 Molecular out-of-plane rotation around the N-N axis at 96 cm^{-1} .

M3 Molecular translation at 114 cm^{-1} .

4.2 Zone I and II: Octahedral and perovskite modes

In this chapter, we studied Zone I and II of the Raman spectrum of $FAPbI_3$, which have not been investigated in the literature. Zone I or the low-frequency zone contains the modes of the octahedron PbX_6 . This zone is defined in a frequency range from 10 to 50 cm^{-1} for iodide containing compounds and from 10 to 65 cm^{-1} for bromides [65]. Zone II or medium frequency zone has information on the response of the inorganic framework to the cation rotation and translation.

The interpretation of this part of the spectrum gives us tools to answer the following questions. A review of the literature on $FAPbI_3$ is presented in Chapter 2.1.6.

1. $FAPbI_3$ is used indistinctly in the states as-synthesized and thermally recovered, with stability in a time frame of 1 day and 20 to 30 days, respectively. Does the same phase correspond to both states?
2. It is agreed in literature that the structure of $FAPbI_3$ at high temperature (180°C) is ideal cubic ($Pm\bar{3}m$). Is this structure the same at RT or is there a phase transition?
3. What is the trigger and the mechanism of the transition $\alpha \rightarrow \delta$?
4. Why does the recovered sample have higher stability?

The detected polymorphism is composed by 3 photo active phases and 1 non photo active. These phases are described in the next sections as follows: *Chapter 5.1* presents the polymorphism, *Chapter 5.2* describes the "as synthesized" or "initial" α_i , *Chapter 5.3*, the degraded δ and α_δ , and *Chapter 5.4*, the thermally recovered α_{rec} and PbI_2 . In these sections, the attribution of the corresponding structures was supported by following the phase-transitions as presented in Table 4.1: a) temperature-driven phase transition $\alpha_i \rightarrow \alpha_{HT}$, b) time-driven phase transition $\alpha_i \rightarrow \alpha_\delta + \delta$, and c) temperature-driven phase transition $\alpha_\delta + \delta \rightarrow \alpha_{HT} \rightarrow \alpha_{rec} + PbI_2$. Here, α_{HT} corresponds to the high temperature state, which has been identified in literature as cubic $Pm\bar{3}m$ at 180°C. Finally, a summary of the main findings is presented in *Chapter 5.6*.

	Variable	Initial state	Treatment	Final State
a)	T°	α_i	$\xrightarrow[20^\circ C]{200^\circ C}$	α_{HT}
b)	time	α_i	1 day	$\alpha_\delta + \delta$
c)	T°	$\alpha_\delta + \delta$	$\xrightarrow[20^\circ C]{200^\circ C}$	$\alpha_{rec} + PbI_2$

Table 4.1: Scheme of the phase-transitions: high temperature structure (α_{HT}), as-synthesized (α_i), thermally-recovered (α_{rec}), and degraded (α_δ). Secondary phases, δ and PbI_2 are shown for clarification.

4.2.1 Polymorphism of $FAPbI_3$

As presented in Chapter 2.1.6, the as-synthesized $\alpha_i - FAPbI_3$ crystal undergoes a phase transition, degrading into a non-photo-active state. This degraded state can be recovered into a photo-active polycrystal via annealing. Microscope captures are present in Fig. 4.5. They are representative of each state but not correlative at the same point.

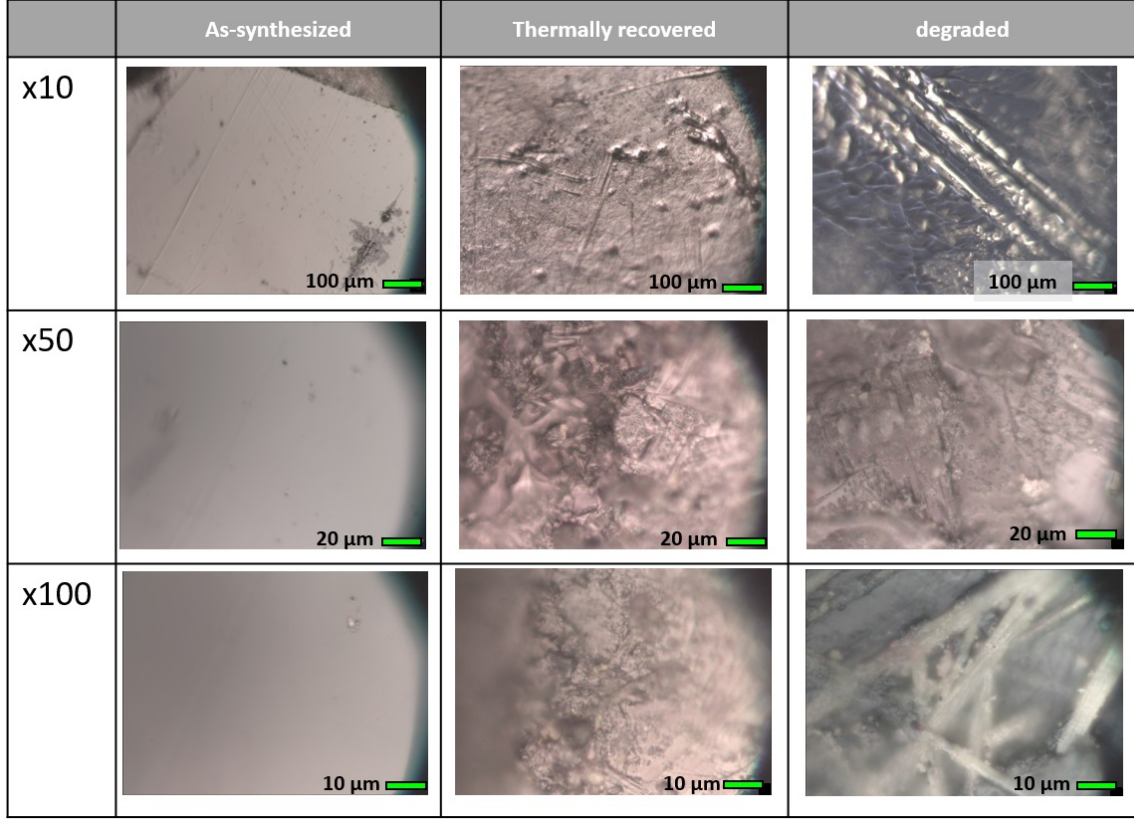


Figure 4.5: Microscope captures with different objectives (10x, 50x and 100x) of $FAPbI_3$: as-synthesized, thermally recovered and degraded.

From an visual inspection, all polymorphs differ one from another. We performed micro-Raman spectroscopy with an objective of 100x to clearly detect all phases present en each state, as shown in Fig. 4.6. As previously commented, we found the following phases:

- As-synthesized: α_i
- Degraded: $\alpha_\delta + \delta$
- Thermally recovered: $\alpha_{rec} + PbI_2$

Comparing the spectra, we noticed the same pattern of α_i in the photoactive phases of the degraded and recovered states. The notation α_x refers to this fact, remarking the shared photoactive nature and the cubic disposition. The normalized PL signals are presented in Fig. 4.7.

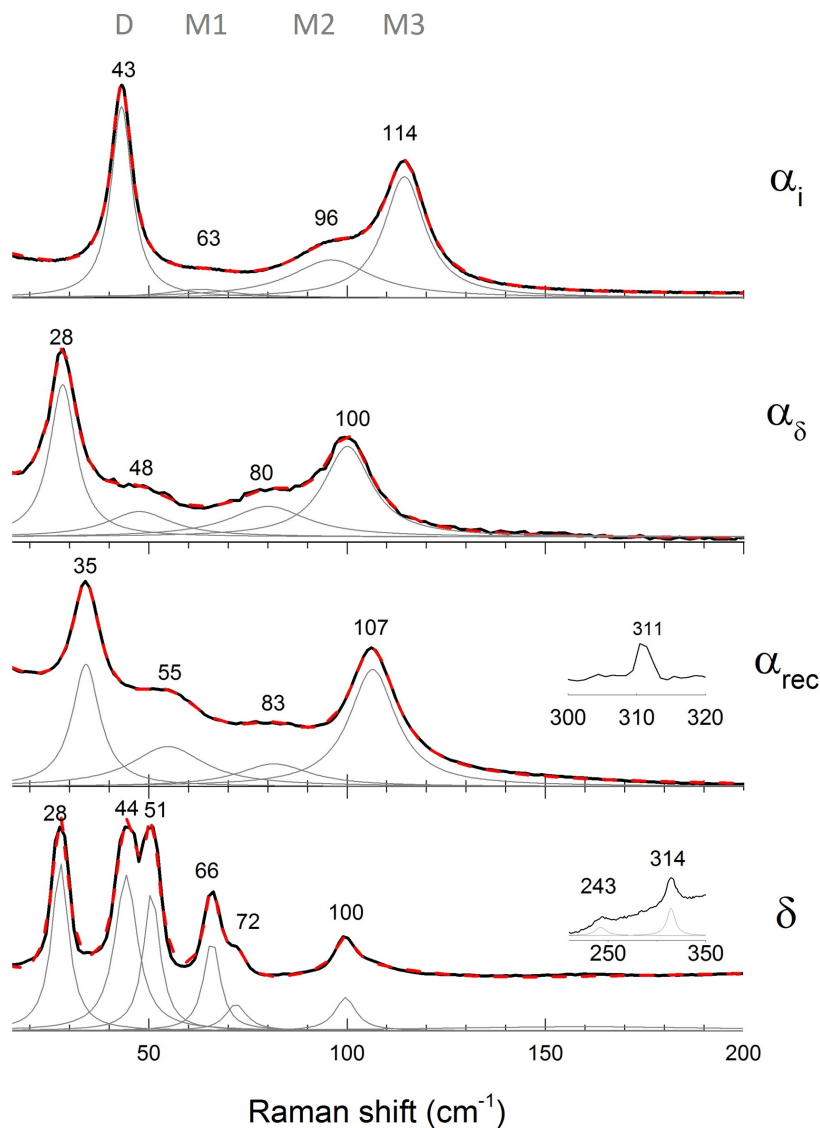


Figure 4.6: Raman spectra of $FAPbI_3$ polymorphism acquired at RT. The black lines indicate experimental data, while the red dotted lines, the resulting fitted curves obtained from the superposition of Raman modes shown as Lorentzian-functions in gray.

The Raman spectra of the α_δ and α_{rec} phases show 3 main distinctions compared to α_i : (i) a red-shift, (ii) variation in the intensity ratio between M2 and M3, and (iii) the appearance of additional mode at 311 cm^{-1} in the α_{rec} -spectrum.

(i) The red-shift of the Raman spectrum suggests a weakening of the Pb-I bond, which is a consequence of a variation either in the bond length or angle. This is also supported by the PL shifting.

(ii) As presented in Chapter 4.1, M2 and M3 modes correspond to molecular rotation: in-plane for M2 and out of a plane for M3. This I_{M2}/I_{M3} ratio can be related to stability as presented in Table 4.2. This is based on the volumetric changes caused by M3 compared to all other modes that are active in the molecular plane. α_δ^* -phase corresponds to the stable as-synthesized yellow crystal described in Chapter 4.2.1.

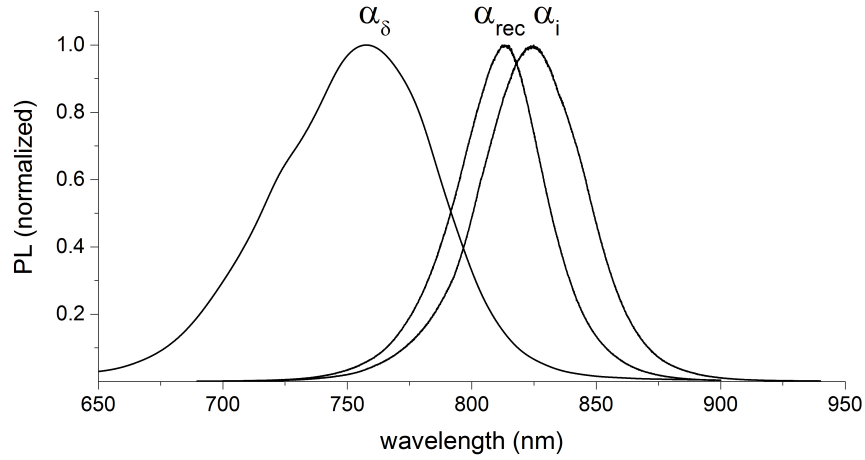


Figure 4.7: PL signal of the $FAPbI_3$ polymorphs at RT: α_i (824 nm), α_δ (765 nm) and α_{rec} (814 nm).

Phase	I_{M2}/I_{M3}	Stability
α_i	0.22	Unstable. 1 day
α_δ	0.83	Unstable. 7 days
α_{rec}	1.77	Unstable. 20-30 days[45]
α_δ^*	8.98	Stable

Table 4.2: Correlation between $FAPbI_3$ phase stability in ambient air and intensity ratio of Raman modes M2 and M3. The term "stable" considers the invariability of the Raman spectrum for more than 10 weeks.

(iii) The additional peak at 311 cm^{-1} in α_{rec} -spectrum also appears in the δ -phase at 243 and 314 cm^{-1} . These correspond to the modes M5 and M6: symmetric and asymmetric out-of-plane bending of FA^+ . The absence of these modes in the spectra of α_i and α_δ could be either veiled due to PL or inactive. In the last case, it may be the result of static hydrogen atoms, which govern these modes.

4.2.2 As synthesized α_i – $FAPbI_3$

As presented in Chapter 2.1.3, the structure of the α -phase is still discussed in the literature. Here we determine the structure of the α_i -phase by comparison of the Raman spectra with the α_{HT} -phase. As agreed in the literature, the α_{HT} -phase is stable at 180°C and possesses a primitive cubic cell ($Pm\bar{3}m$). By contrast, the α_i -phase is highly unstable, pointing towards a distorted structure. Following this reasoning, we performed temperature-dependent Raman spectroscopy from 25°C to 200°C aiming to identify the structural differences between the two boundary states. The spectra are shown in Fig. 4.8.

In the range from 20°C to 100°C , the 4 characteristic Raman modes of α_i (Chapter 4.1.3) slightly broaden and red-shift. Beyond 100°C only M4 remains, broadening and blue-shifting, while the rest of the modes become inactive.

A stepwise conjugated variation of the Raman shift and the Full Width at Half Maximum and Raman shift with temperature may indicate phase transition in perovskites [84]. Hence,

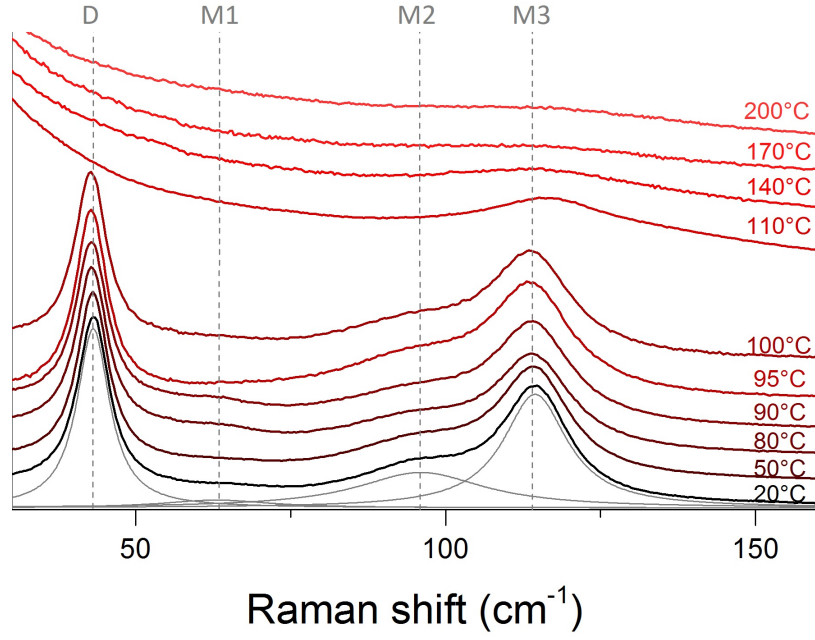


Figure 4.8: Raman spectra of phase transition $\alpha_i \rightarrow \alpha_{HT}$ in $FAPbI_3$ in ambient air. Lorentzian-fitted Raman peaks for the spectrum RT are indicated by gray curves and identified at the top as MX, with $X \in [1, 4]$.

there may be a structural reorganization between 100°C and 110°C. In the following, we determine and characterize the structure of α_{HT} , analyze the physical justification of this transition, and conclude the structure of the α_i -phase

Structure of α_{HT} : We have confirmed by Raman spectroscopy the attribution of $Pm\bar{3}m$ symmetry for this phase. According to group theory, LHPs with this symmetry only present active Raman modes for low-coupled and strictly molecular vibrations [73]. This is experimentally supported in the case of $\alpha - MAPbI_3$ [65, 132]. In other words, modes from Zone I and Zone II are inactive, except for high-frequency modes close to Zone III (below 200 cm^{-1} for $FAPbI_3$).

The mode inactivation can be explained as follows.

- M1** Octahedral twist is an asymmetric vibration, which by definition, should be inactive in a symmetric system.
- M2-3** the molecular rotation does not change the polarizability in a symmetric system because the center of charge is almost static: M2 constrains the vibration in the plane where FA^+ is located, and in M3, the center of charge is kept within the rotation axis.
- M4** the translation mode involves the displacement of the molecular cation and consequently I ions, resulting in a shift of the charge center. The mode gets broader with the amplitude reduction of polarization due to the loss of preferential direction.

Physical justification:

Phase transitions in perovskites can be caused by changes in the motion of the organic cation and its interaction with the lattice[19, 54]. The atomic displacement and reorganization in $FAPbI_3$ at temperatures below 100°C are not coupled. On the one hand, I^- atoms displace within a characteristic time of 10 ps [16] while, on the other hand, the FA^+ cations rotate around its N-N axis at 2 ps [129]. This leads to the activation of Raman modes in the α_i -phase due to the lowering of symmetry. At temperatures higher than 110°C, the spherical rotation of the FA^+ cations and the faster response of I ions simulates symmetric structure statistically. This causes the polarizability of the structure does not vary with the vibration and, consequently, the Raman modes become inactive [73, 132]

This phase transition $\alpha_i \rightarrow \alpha_{HT}$ is also measurable by temperature-dependent PL and single crystals XRD, as shown in Fig. 4.9 and 4.10. In PL, there is a slope variation of the wavelength shift from 90°C to 110°C. In XRD, we discovered a shrinking of the lattice constant at heating from 80°C to 120°C. Table 4.3 shows the lattice parameter of the SCs obtained by a Le Bail fitting using cubic $Pm\bar{3}m$ symmetry.

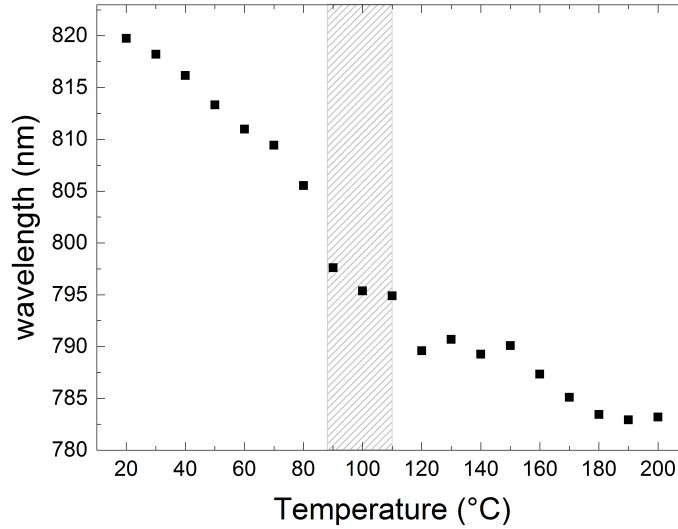


Figure 4.9: Temperature dependence of PL signal position of the transitions $\alpha_i \rightarrow \alpha$.

Table 4.3: Results of the Pawley refinement using cubic $Pm\bar{3}m$ space group for the patterns presented in Fig.4.10.

T° (°C)	Lattice parameter a ($Pm\bar{3}m$)
30	6.364
80	6.385
120	6.375
160	6.397

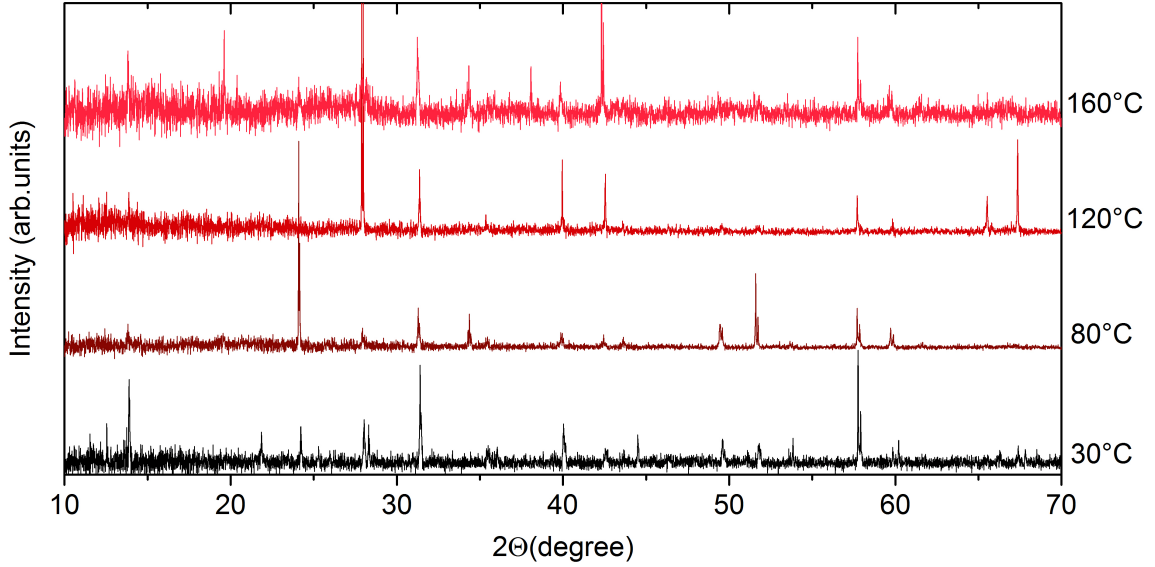


Figure 4.10: Temperature dependent XRD measurements of α_i - $FAPbI_3$ SCs.

We summarize here the material properties that agree with the critical range of temperature.

90°C-110°C Variation in the wavelength shift tendency with the increasing temperature.

80°C-120°C Shrinking of lattice parameter in SC XRD.

97°C According to MD calculations, there is a weak anharmonicity of I^- displacement existing in $FAPbI_3$ below 97°C, diverting the structure from the ideal configuration [17].

100°C-125°C Optimum temperature for the single crystal growth by inverse temperature crystallization method[104]

87°C Long-term stability of $FAPbI_3$ crystals inside the mother liquor [112].

113°C Phase-transition of FAI into the cubic form [97].

Structure of α_i -phase: Since α_i presents active modes, we identify a distorted structure with cubic symmetry. Furthermore, the distortion is present in form of highly displaced I^- atoms and low molecular rotation.

As presented in Chapter 2.1.6, MD calculations suggest a cubic body-centered cell with $Im\bar{3}$ symmetry for $FAPbI_3$ at RT [16]. However, characteristic peaks of this symmetry, for instance at 22.5° and 26.5°, are not reflected in our SC XRD. There are two possible reasons for that: (i) XRD considers the average positions of the bulk material, neglecting the instantaneous dynamics, and (ii) the molecular ordering is not influential if the position of the molecule in the unit cell is constant. This was corroborated by modeling XRD patterns in the software VESTA. Therefore, the structure of α_i is probably cubic $Im\bar{3}$, with head-to-tail organization of the FA^+ molecules [4, 112] associated with the I^- displacements.

To summarize, $\alpha_i - FAPbI_3$ presents a cubic $Im\bar{3}$ symmetry due to the anharmonicity of iodine displacements and molecular organization. The material undergoes a phase transition around 100°C to 110°C, from where it transforms into the ideal perovskite with $Pm\bar{3}m$ symmetry. The active rotation of FA^+ ions results in geometrical sphericity, which provides higher crystal symmetry and Raman modes inactivation.

4.2.3 Degraded $\alpha_\delta + \delta - FAPbI_3$

The yellow crystal of $FAPbI_3$ is usually obtained at RT from the α_i -phase within a time frame of 1 to 10 days depending on the storage, as a consequence of the internal strain of the α_i -phase.[141]. This yellow form remains stable for more than 10 weeks when stored in vacuum. During the transformation, the SC shape remains unchanged.

When placing a yellow SC under the microscope, three different zones can be observed: (i) yellow needles, δ , (ii) a dark matrix, α_δ , and (iii) an intermediate zone comprehending small yellow round crystals of ca.1 μm . Each zone is analyzed through Raman spectroscopy (see Fig. 2.9).

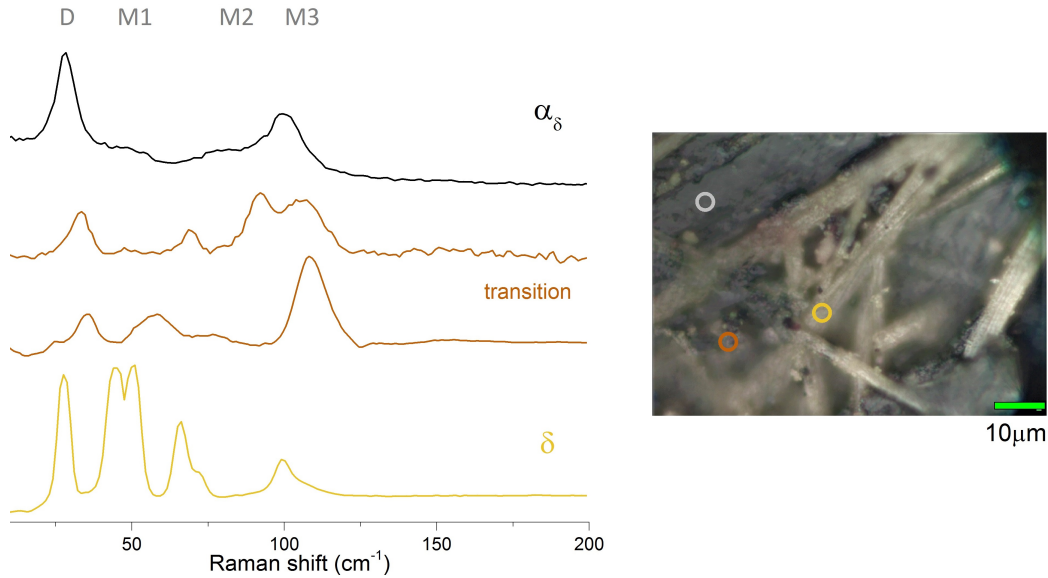


Figure 4.11: Raman spectra of the polymorphism of degraded $FAPbI_3$ SC associated by color to the measurement point shown in the microscope image (magnification x100).

(i) **Yellow needles, δ :** The Raman spectrum presents 6 peaks in the low-frequency range below 200 cm^{-1} . M1 and M4 positions remains the same as α_δ , which is red-shifted compared to α_i (Fig. 4.6). M2 and M3 are split into two peaks each one: at 44 and 51 cm^{-1} , and at 66 and 72 cm^{-1} , respectively. The splitting and red-shift are a consequence of the merged octahedra in the hexagonal $P6_3mc$ lattice, which interconnect by faces along with the $\langle 001 \rangle$ directions. According to SC XRD analysis, the cell parameters of the hexagonal lattice are $a=8.660\text{\AA}$ and $c=7.902\text{\AA}$ [112]. This means two different Pb-I bonds lengths, 3.190 $\text{\AA}$ and 3.240 $\text{\AA}$, longer than the Pb-I=3.182 $\text{\AA}$ from the cubic cell of α_i ($a=6.364\text{\AA}$, Table 4.10). Additionally, each FA^+ molecule affect via molecular reorientation of three double-merged octahedra units and vice versa, as seen in Fig. 2.9.

(ii) Dark matrix, α_δ : As previously stated, the Raman spectrum presents the 4 characteristic modes of α_i -phase (Fig. 4.6), red-shifted is by 15 cm^{-1} . The most probable reason for this shift is the variation of the Pb-I bond angles, producing distortion. This effect is congruent with the blue-shift of the PL signal, which has a wavelength around 60 nm shorter than the α_i -phase (see Fig 4.7). Another possible reason is the expansion of the unit cell. However, the density of δ - and α_δ -phase is similar: 4.10 g/cm^3 ([112]) and 4.00 g/cm^3 ([129]), respectively. In this way, α_δ expands synchronously with the apparition of the δ -phase, which in turn predicts a neglectable increment of the lattice constant.

The distortion of the lattice predicts an increase in the internal strain. Therefore, the release of strain is discarded as a mechanism for enhanced stability. For this reason, it can be concluded that higher stability of the α_δ -phase is a consequence of another reason: the constriction of volumetric displacement of FA^+ . The latter is expressed as a hindering of the M3 intensity, i.e, the molecular out-of-plane rotation around the N-N axis.

(iii) Transition: The small round yellow crystals show different Raman spectra, indicating differed advancing of the transition. Two examples are shown in Fig. 4.11. These spectra present a red-shift of M1 and M4 of ca. 13 cm^{-1} (respect to the α_i -spectrum) and sharpening and splitting of M2 and M3. These characteristics likely represent the partial merging of the octahedra, corresponding to the intermediate states of the transition $\alpha_i \rightarrow \delta$.

With the information from the Raman spectroscopy, we can interpret the temporal transition α_i to δ as follows. Initially, the cubic $\alpha_i - FAPbI_3$ distorts due to the volumetric rotation of the cations, becoming α_δ . The nucleation of the δ -phase starts at the most defective sites of the α_δ -matrix. There, some octahedra expand and merge, encircling two organic cations per unit cell. This starts the growth of a second phase as different crystals. The octahedra continue merging in the vicinities, leading to the consolidation of the hexagonal structure. Thus, the yellow needles of a pure δ -phase grow.

Another way to obtain a yellow crystal of $FAPbI_3$ is directly synthesized via heating of the 1M $FAPbI_3$ +GBL solution at 70°C overnight. The shape of the resulting crystal is needle-like, an elongated and thin structure. Under the microscope, it presents the 3 zones described above. The only difference is found in the α_δ -spectrum: a smaller red-shift of 9 cm^{-1} (Fig. 4.12). The stability of this state is related to the likely high distortion level, which is in turn detrimental for the intensity of PL decreased several orders of magnitude with respect to α_i .

4.2.4 Thermally recovered $\alpha_{rec} - FAPbI_3 + PbI_2$

Raman The even higher stability of the α_{rec} -phase in the recovered sample can be explained by a stress release which is known to improve the stability of hybrid perovskites [141]. The observed expanded lattice of the α_{rec} -phase (see Fig. S9) corresponds to the release of isotropic compressive stress. This may be bound exactly with the formation of PbI_2 which is appreciably denser: 5.36 g/cm^3 . In a turn, lead iodide has the same structural fragments as delta-phase (face shared PbI_6 -octahedra) that gives rise to the PbI_2 formation in compressing environment during heating. Moreover, the fact that the mixture of α_δ /

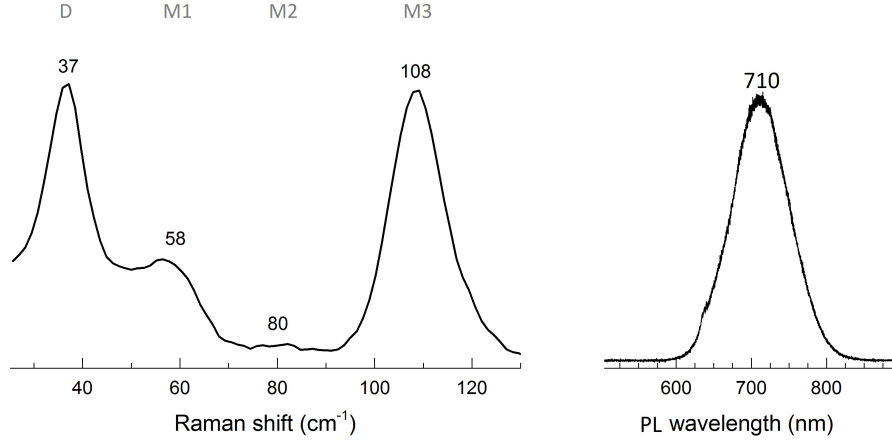


Figure 4.12: Raman spectrum and PL signal of $\alpha_\delta * -FAPbI_3$. This corresponds to the α_δ -phase that appears in yellow needle-like $FAPbI_3$ crystals.

δ phases undergoes the solid phase transformation causes multiphase interfaces facilitating nucleation of PbI_2 . A remarkable suppression of the “out-of-plane rotation around N-N axis” mode is also observed in the α_{rec} -phase, becoming almost inactive as in the case of the isolated molecule. This points to a larger unoccupied volume for the free rotation of the molecule, uncoupling to the surrounding octahedra. Thermally recovered SC was analyzed by Raman spectroscopy and compared to the other polymorphs of $FAPbI_3$ at RT, as shown in Fig.4.6.

The Raman spectrum of the α_{rec} -sample shows the same 4 modes of α_i with 3 distinctions: (i) a red-shift of 9 cm^{-1} , (ii) a increase in the intensity ratio between M2 and M3 from 0.22 (α_i) to 1.84 (α_{rec}), and (iii) the appearance of additional mode at 311 cm^{-1} .

The third characteristic is the peak at 311 cm^{-1} of α_{rec} -spectrum, which also appears in the δ -phase at 243 and 314 cm^{-1} . These correspond to the modes “symmetric and asymmetric out-of-plane bending of FA^+ ” [48]. In the spectra of α_i and α_δ , the absence of this mode could be either veiled due to luminescence or inactive. In the last case, it may be the result of static hydrogen atoms, which govern these modes.

In contrast with the polymorphs of the α -phase, the δ -phase can be detected and distinguished by XRD. In literature, there are several studies following the annealing of the degraded sample [45, 49, 112, 129]. Thus, we consider a second process: after the SC is thermally recovered, it eventually degrades and can be again annealed. This second transition is followed by in-situ powder XRD the transition to $\alpha_\delta + \delta \rightarrow \alpha_{HT} \rightarrow \alpha_{rec} + PbI_2$, as presented in Fig. 4.13.

At RT, the degraded sample shows the expected hexagonal lattice, together with the recovered sample remnants: cubic patterns and PbI_2 . The δ -phase fully disappears between 140°C and 180°C , which coincides with an endothermic peak around 160°C detected by differential scanning calorimetry [49]. After cooling, the sample contains cubic $FAPbI_3$ (α_{rec}) and PbI_2 . The presence of this non-photoactive PbI_2 works as a superficial trap, decreasing the amplitude of the PL signal about tenfold as compared to the α_i under the same illuminating conditions.

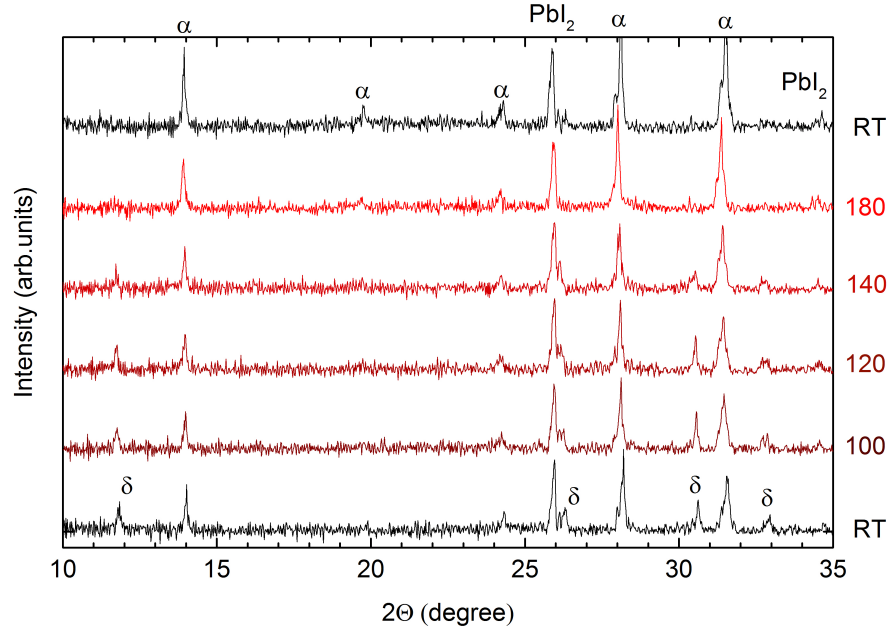


Figure 4.13: Temperature dependent XRD analysis of twice-degraded $FAPbI_3$ powder. The transition to the recovered state starts above 140°C and finishes by 180°C.

Powder XRD cannot detect the transition $\alpha_{rec} \rightarrow \alpha_{HT}$. According to temperature dependant PL, the wavelength variation presents a disruption in its tendency from around 110°C (Fig. 4.14). This coincides with the transition α_i to α_{HT}

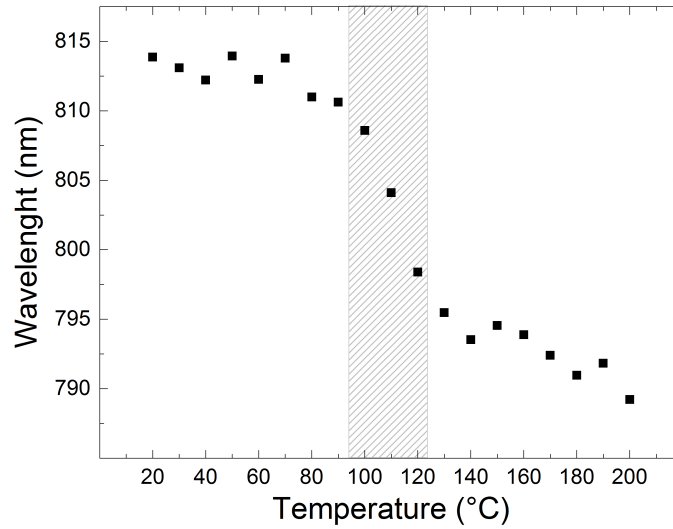


Figure 4.14: Temperature dependence of PL position of the transition $\alpha_{rec} \rightarrow \alpha_{HT}$

4.2.5 Summary

We distinguished in our experiments three polymorphs of the photo-active α - $FAPbI_3$ existing at RT: as-synthesized (α_i), degraded (α_δ), and thermally recovered (α_{rec}). They mostly differ in the level of distortion, product of a secondary phase: δ for the degraded sample and PbI_2 for the thermally recovered one. The Raman spectrum of the α_i -phase points at the highest activity of the Raman mode "molecular rotation around N-N axis", which is likely a main factor in the structural instability.

We proposed the $\alpha_i - FAPbI_3$ crystals to have cubic $Im\bar{3}$ structure at RT. Herewith, the FA^+ molecules are organized in a head-to-tail fashion and the displacements of I- ions proceed slower than the FA^+ displacement. Raman spectroscopy disclosed a transition of this distorted phase into the ideal perovskite with $Pm\bar{3}m$ symmetry around 100-110°C, where the corresponding Raman modes become inactive.

We demonstrated that the understanding of vibrational dynamics in hybrid perovskites could bring additional assets in the development of new and stable structures.

4.3 Zone III: Molecular modes

In this chapter, we studied Zone III or the high-frequency zone of the Raman spectrum of various LHPs. This zone is related to molecular modes. They coincide with the modes of isolated molecules, with any discrepancy attributed to the interaction between the organic cations and the inorganic frame. For FA^+ -containing compounds, it starts at 500 cm^{-1} , while for MA^+ -containing compounds it starts at 800 cm^{-1} .

The main question to answer in this chapter is: do LHPs have hydrogen bonds?

LHPs have been attributed to hydrogen bonds to be responsible for several properties, as presented previously in Chapter 2.1.4. In literature, they are ascribed when the distance between H and the halide is less than the sum of the corresponding Van der Waals radii [4, 39, 64, 65, 81, 86, 100, 103, 114, 114, 123, 129, 131]. However, the calculation of this radius in crystals is highly uncertain due to the difficulty to determine it and the existence of additional supramolecular aggregation [107].

The method proposed to determine the existence of hydrogen bond was employed in literature for water and alcohols and is based on the apparition of an additional peak related to a charge transfer state [2]. Chapter 6.1 presents the calculated Raman modes of FA^+ and MA^+ . In Chapter 6.2, the method is proved in precursor salts *MAI* and *FAI*. Chapter 6.3 shows the application of the method in *FAPbBr₃* and *MAPbBr₃*. A comparison with other LHPs is analyzed in Chapter 6.4. Chapter 6.5 provides a discussion of the results, which are summarized in Chapter 6.6.

4.3.1 Attribution of Raman modes of MA^+ and FA^+ isolated molecules

Analogous to Chapter 4.1, DFT calculations were performed to attribute the Raman modes of the isolated molecules, MA^+ and FA^+ . We attributed the symmetry group of each mode and corroborated it according to the irreducible representation of Raman modes of the molecule. In the case of FA^+ , the molecule has a C_{2v} symmetry, leading to $\Gamma = 7A_1 + 2A_2 + 6B_1 + 3B_2$ [60]. In the case of MA^+ , the C_{3v} symmetry results in $\Gamma = 5A_1 + A_2 + 6E$ [79]. The Raman mode of A_2 symmetry is not analyzed due to the inactive nature of the isolated molecule. It depicts molecular torsion. The results are presented in Table 4.4 and Table 4.5, with a correlation with literature data of FA^+ [60] and *MAPbI₃* [65], respectively.

Raman modes of FA^+

Raman modes of FA^+ present the following characteristics. Modes 1 to 6 occur out of the molecular plane, mainly by the hydrogen atoms, except mode M3 at 556 cm^{-1} . From mode 7 to 18, all vibrations occur in the molecular plane.

We also distinguished the pair of hydrogen involved in terms of closeness to the C-H bond, as presented in 4.15. The closest are denoted H_C , while the farthest H_F . Their different displacement and molecular symmetry are relevant in the determination of hydrogen bonding. In modes M1, M5, M7, and M8, the atoms with the highest displacement are the H_C pair. While in modes M4, M6, and M10 the most mobile pair is H_F .

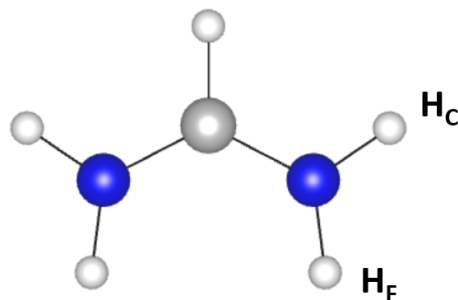


Figure 4.15: Classification of hydrogen atoms in the FA^+ molecule.

The pattern of our calculated Raman spectrum and the description of the modes generally agree with the only data found in literature [60]. However, there are two main differences to point. First, the modes M1, M2, M3, M7, M9, and M11 have different sequences. Exactly this causes high Δ values, however, the majority of modes befall in a difference in Raman shift of less than 7%. And second, the activity or intensity of some modes diverges. As an example, our calculations show that the mode with the highest activity is M2, whereas in literature it is M3. These differences apparently originate from the dissimilarity in the functional used: Kucharska *et al.* performed Gaussian calculations where we combined Gaussian and Plane Wave ones.

Table 4.4: DFT calculated modes of the isolated FA^+ . Symmetry group is assigned based on the irreducible representation of Raman modes of the molecule with C_{2v} symmetry: $\Gamma = 7A_1 + 2A_2 + 6B_1 + 3B_2$. The pair of H atoms with the highest displacement in the vibration is denoted by: H_C , closest to the H bonded to the C atom, H_F , farthest from the C atom, B if both displace similarly, or blank, if they are not relevant. The relative difference between this work calculations (f_1) and the reference data(f_2) is stated by $\Delta = 1 - f_2/f_1$ (%).

Mode	Description of FA^+ Raman modes	Sym. Group	H atoms	Mode frequency (cm^{-1})		
				This work	ref [60]	$\Delta(\%)$
1	NH_2 asym. wagging	A_2	H_C	478	533	-11.5
2	NH_2 asym. wagging	B_2	B	548*	601	-9.7
3	NH_2 -C- NH_2 sym. bending	A_1	B	556	521*	6.3
4	NH_2 asym. wagging	A_2	H_F	598	587	1.8
5	NH_2 asym. wagging	B_2	H_C	675	718	-6.4
6	NH_2 asym. wagging + C-N stretching	B_2	H_F	1052	1047	0.5
7	NH_2 scissoring + C-H wagging	B_1	H_C	1079	1084	-52.5
8	NH_2 scissoring + C-H stretching	A_1	H_C	1150	1130	1.7
9	NH_2 rocking + C-H wagging	B_1		1376	1084	21.2
10	NH_2 rocking+ C-H stretching	A_1	H_F	1384	1419	-2.5
11	C-H bending + scissoring NH_2	B_1	B	1610	1388	13.8
12	NH_2 scissoring	A_1	B	1688	1741	-3.1
13	C-H bending + C-N stretching + NH_2 scissoring	B_1	B	1762	1789	-1.5
14	C-H stretching	A_1		3091	3208	-3.8
15	NH_2 sym. stretching	B_1	B	3388	3552	-4.8
16	NH_2 sym. stretching	A_1		3404	3566	-4.8
17	NH_2 asym. stretching	B_1	B	3525	3669	-4.1
18	NH_2 asym. stretching	B_1	B	3527	3671	-4.1

Raman modes of MA^+

There are no reported calculations for the isolated methylamine molecules but there are for $MACl$, $MABr$, $MAPbBr_3$ and $MAPbI_3$ salts [38, 65, 79, 100, 131]. For the sake of comparison, we present the calculated Raman modes of cubic $Pm\bar{3}m$ $MAPbI_3$ at -173°C and the relative difference with our calculations. The group symmetry of each mode was already attributed $MACl$ [79] and corroborated by us.

In this case, the calculations for MA^+ and $MAPbI_3$ coincide in frequency ($\pm 9 \text{ cm}^{-1}$) and pattern of the spectrum, giving place to an adequate interpretation of MA^+ containing compounds. It is interesting to remark the low value of Δ , which points out a neglectable interaction between the molecule and the surrounding octahedra. These data will be used below as a basis for the interpretation of the Raman spectra measured for MAI , $MAPbI_3$, and $MAPbBr_3$.

Table 4.5: DFT calculated modes of the isolated MA^+ . Symmetry group is assigned based on the irreducible representation of Raman modes of the molecule with C_{3v} symmetry: $\Gamma = 5A_1 + A_2 + 6E$. Torsion mode of A_2 symmetry is not active in the isolated molecule and therefore is not part of this analysis. The relative difference between this work calculations (f_1) and the reference data(f_2) is stated by $\Delta = 1 - f_2/f_1(\%)$.

Mode	Description of MA^+ Raman modes	Sym. Group	Mode frequency (cm^{-1})		
			Our DFT MA+	Ref[65] $MAPbI_3$	Δ (%)
1	C-N asym. bending	E	954,966	876,909	8.2, 5.9
2	C-N stretching	A_1	1004	1007	-0.3
3	C-N asym. bending	E	1292,1314	1215,1234	6.0, 6.1
4	CH3 sym. bending	A_1	1469	11378	6.2
5	CH3 asym. bending	E	1492, 1501	1418, 1425	5.0, 5.1
6	NH3 sym. bending	A_1	1582	1464	7.5
7	NH3 asym. bending	E	1680, 1694	1542, 1558	8.2, 8.0
8	CH3 sym. stretching	A_1	3010	2971	1.3
9	CH3 asym. stretching	E	3118,3124	3067,3074	1.6, 1.6
10	NH3 sym. stretching	A_1	3194	3087	3.4
11	NH3 asym. stretching	E	3278,3285	3096,3199	5.6,2.6

4.3.1.1 Proof of work: criterium of charge transfer interaction

We determined the presence or absence of hydrogen bonds under the premise that the involved charge transfer between donor and acceptor must appear in the Raman spectrum [2]. This mode is exclusive to the charge-transfer state and appears additionally to the normal modes.

Analysis of FAI

To prove the usability of our approach, we considered FAI which is known to possess hydrogen bonds at -173°C [97]. At this temperature, the substance has a monoclinic structure with the space group P21/c. According to Petrov et al, the I^- ions are strongly bound to H-C groups and lay in a molecular plane. The thermogravimetry and differential scanning calorimetry have not evidenced any phase transition in FAI below 73°C to 0°C . Below 0°C , the powder XRD patterns are mostly invariant outside the shift due to the thermal contraction [80, 97]. Then, the variation in the Raman spectrum can be attributed to the formation or breaking of intermolecular bonds. Figure 4.16 shows the measurement for FAI powder Raman spectra in a temperature range from -200°C to 25°C . The differences between Raman spectra acquired at temperature extremes are highlighted in Fig. 4.17 and the complete modes attribution is presented in Table 4.6.

The shrinkage of the lattice at decreasing temperature leads to the peak sharpening, variation of relative intensities, and blue-shift of the Raman spectra. Two changes escaped this expected behavior. First, the red-shift of modes M3 and M10, and second, the apparition of an additional peak at the right of M3 (See Fig. 4.17). M3 and M10 are the only modes that involve in-plane displacement of HF atoms, then the red-shift is likely the result of the lengthening of the N-HF bonds. According to the work of Abe and Ito [2], the second

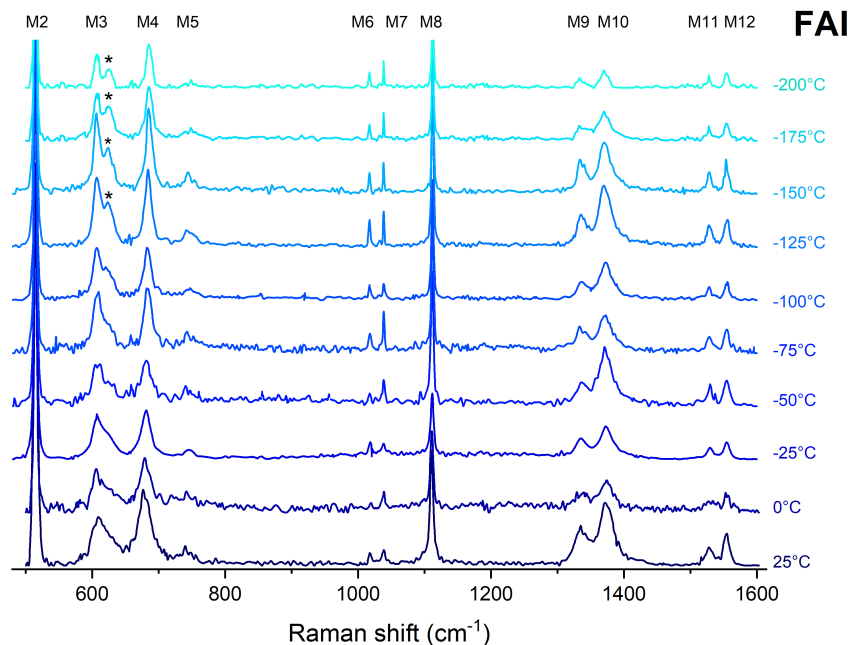


Figure 4.16: Raman spectra of FAI in a temperature range from RT to -200°C

Table 4.6: An attribution of the experimental FAI Raman modes and their attribution according to the DFT calculations of the isolated FA^+ molecule. The correlation has been started with the most intensive mode (*: DFT- 548 cm^{-1} to Exp FAI (25°C)- 514 cm^{-1}). Δ corresponds to the shift in cm^{-1} of FAI(-200°C) and FAI(25°C).

Modes	Description of FA^+ Raman modes	Mode Frequency			
		DFT FA^+	FAI (25°C)	FAI (-200°C)	Δ
2	NH_2 sym. wagging	548*	514*	515	+1
3	$NH_2 - C - NH_2$ sym. bending	556	611	607, 625	-4 (607)
4	NH_2 asym. wagging	598	678	685	+8
5	NH_2 asym. wagging	675	741	748	+7
6	NH_2 asym. wagging + $C - N$ stretching	1052	1018	1018	0
7	NH_2 scissoring + $C - H$ wagging	1079	1038	1038	0
8	NH_2 scissoring + $C - H$ stretching	1150	1110	1112	+2
9	NH_2 rocking + $C - H$ wagging	1376	1335	1335	0
10	NH_2 rocking + $C - H$ stretching	1384	1373	1370	-3
11	$C - H$ bending + NH_2 scissoring	1610	1528	1528	0
12	NH_2 scissoring	1688	1554	1555	+1

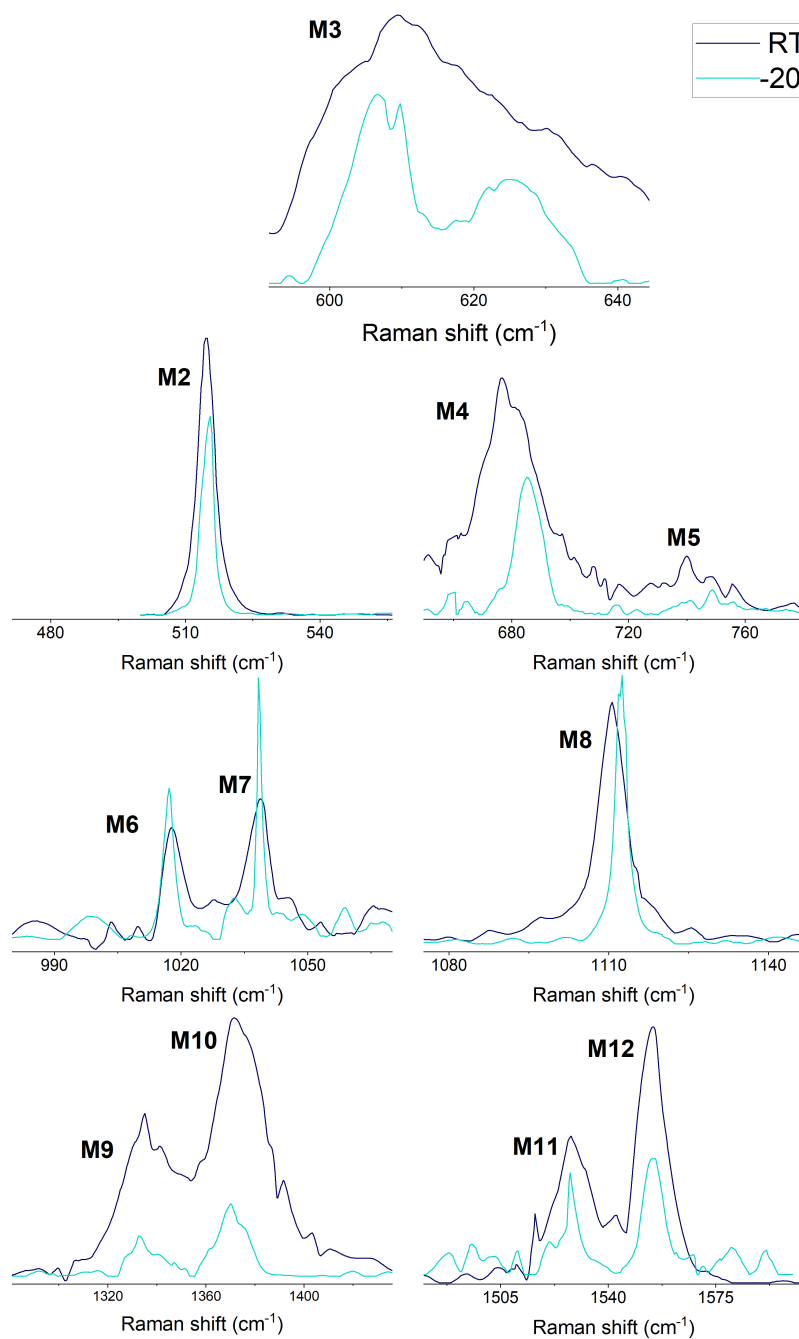


Figure 4.17: Comparison of Raman modes of FAI at RT and -200°C. Mode enumeration correlates to the attribution of Table 4.15

point indicates the presence of hydrogen bonds, which was expected for FAI at low temperatures [97]. The mode M3, located at 611 cm^{-1} (25°C), splits into two modes located at 607 and 625 cm^{-1} (-200°C). At RT, a small hump can be appreciated, differentiating as a secondary peak at -100°C . According to our DFT calculations, this mode corresponds to the $\text{NH}_2-\text{C}-\text{NH}_2$ sym. bending, which involves the displacement of both hydrogen types (H_C and H_F) in an in-plane vibration. Combining these two reasonings, one explanation could be that the hydrogen bonds in the FAI crystal involve the HF atoms.

After the presence of hydrogen bonds in FAI is confirmed at low temperature by Raman spectroscopy, there is still the question to answer: What kind of bonds are those? Despite widely discussed N-H...I bonds in HPs, we propose that in FAI are the N-H...N ones more probable. There are several reasons to state that: nitrogen reveals larger electronegativity (3.04) as compared to iodine (2.66) and has a much smaller atomic radius ($r_N=65\text{ pm}$, $r_I=140\text{ pm}$). The N-H...N bonds are not expected to form in MAI and HPs for geometrical reasons. Further work is needed to clarify this hypothesis.

Analysis of MAI

A different case is MAI. This crystal presents a tetragonal structure at RT with a space group P4/nmm . At -110°C , it overcomes a phase transition into orthorhombic Pbma . Below that temperature, there is no other transition according to thermogravimetry and differential scanning calorimetry [134].

The temperature dependence Raman spectra are presented in Fig. 4.18. Additionally, a comparison between each mode at 25°C and -200°C is shown in Fig. 4.19. The mode attribution, group symmetry, and shift are summarized in Table 4.7.

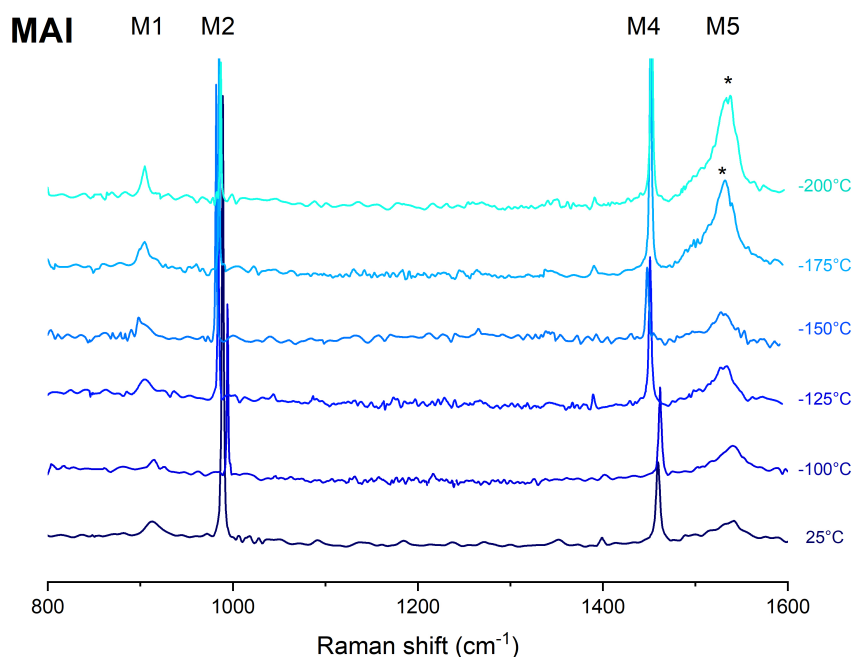


Figure 4.18: Raman spectra of MAI in a temperature range from 25°C to -200°C

As appreciated in Fig. 4.18, there are only 4 modes active in the considered temperature range. From the direct comparison of Raman modes at RT and -200°C , there is no additional

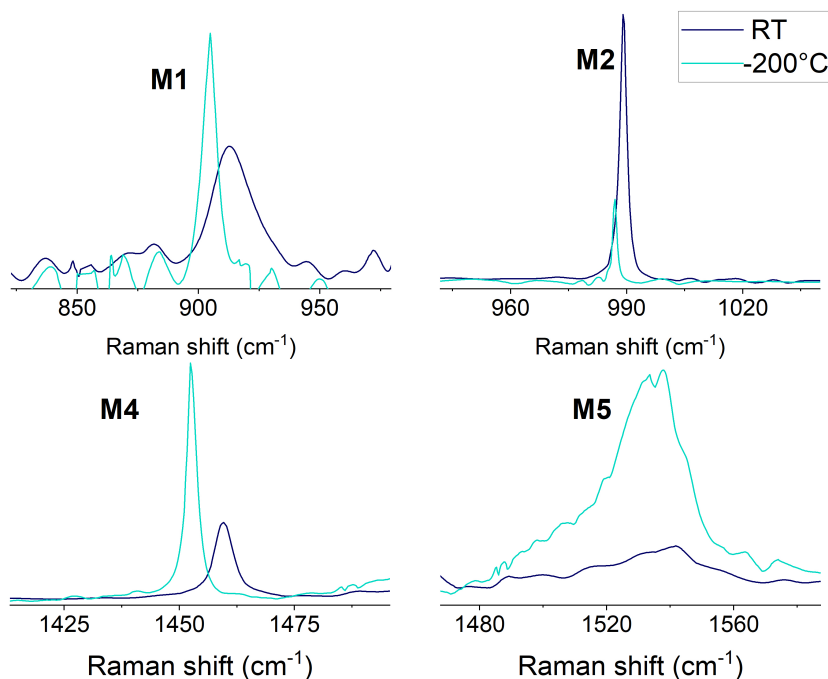


Figure 4.19: Comparison of Raman modes of MAI at RT and -200°C. Mode enumeration correlates to the attribution of Table 4.7

Table 4.7: Experimental MAI Raman modes attribution according to the DFT calculations of the isolated MA^+ molecule. Δ corresponds to the shift of MAI between (25°C) and (-200°C).

Modes	Description of MA^+ Raman modes	Sym. Group	Mode frequency			
			Our DFT MA^+	MAI (25°C)	MAI (-200°C)	Δ
1	C-N asym. bending	E	954,966	913	905	8
2	C-N stretching	A_1	1004	989	987	2
3	C-N asym. bending	E	1292,1314	-	-	-
4	CH3 sym. bending	A_1	1469	1459	1452	7
5	CH3 asym. bending	E	1492, 1501	1514,1535	1509,1535	5,0
6	NH3 sym. bending	A_1	1582	-	-	-
7	NH3 asym. bending	E	1680, 1694	-	-	-

peak, as presented in Fig. 4.19. Moreover, all modes are red-shifted with temperature, as expected from shrinkage. For more information, we studied the evolution of the peak position with temperature. We selected M2 and M4 due to the unambiguity of the peak position. A detailed frequency shift of M2 and M4 is presented in Fig. 4.20.

At temperatures higher than -100°C there are no remarkable changes to notice, apart from a small blue shift ($\sim 4 \text{ cm}^{-1}$), which is expected from the lattice shrinkage at cooling. At cooling below -100°C, the modes reveal a red-shift ($\sim 10 \text{ cm}^{-1}$), which is related to a lattice reorganization with longer bonds. As previously mentioned, a phase transition takes place at -110°C from tetragonal to orthorhombic. The redshift continues until a temperature between -150°C and -175°C. Below that point, the phase is stabilized and again the lattice shrinks with cooling. It can be suggested then the consolidation of intermolecular

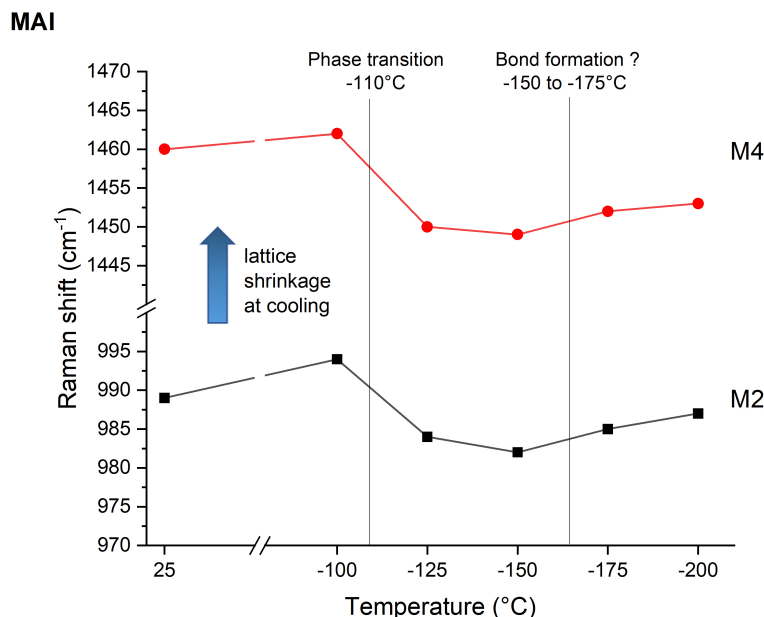


Figure 4.20: Variation of Raman shift versus temperature of M2 and M4, where the vertical line indicates the temperature of phase transition [14] and possible bond formation.

interaction in this range of temperature. The nature of this interaction is hinted as a hydrogen bond by the increase in the intensity of mode M5, related to CH_3 asymmetrical bending and indicated by * in Fig 4.18. However, as it is not accompanied by an attendant peak occurrence, we cannot directly attribute this change to a hydrogen bond formation. For more information, it is possible to perform an extended measurement that covers NH_3 related modes, especially for stretching modes ($>3000\text{ cm}^{-1}$), since NH_3 hydrogen atoms are expected to be involved in the bonding.

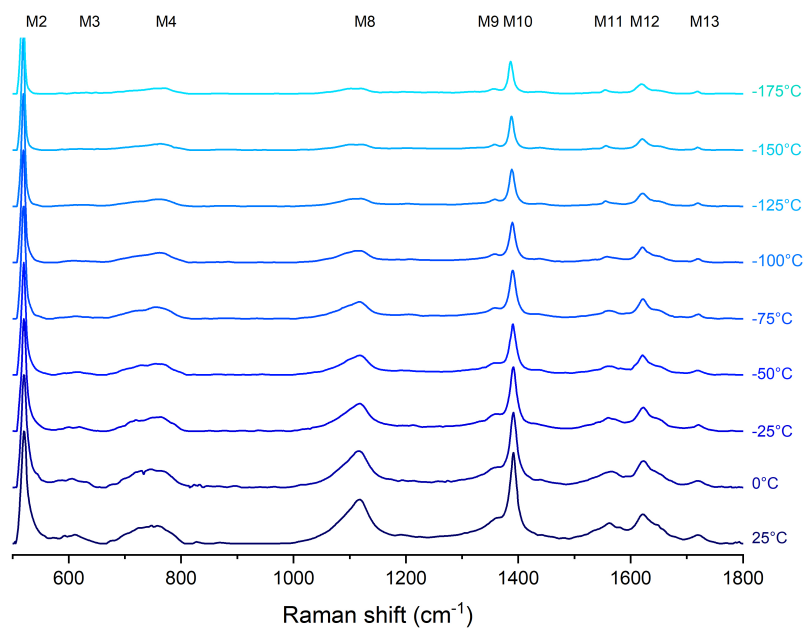
In conclusion, the criterium of charge transfer interaction applied to Raman spectroscopy works for these compounds and can be used for hybrid halide perovskites. Additional peaks due to hydrogen bonding can also be present for bending modes at frequencies between 1000 to 2000 cm^{-1} , which leads us to identify the involved hydrogen pair in the bonding.

4.3.1.2 Application to hybrid halide perovskites

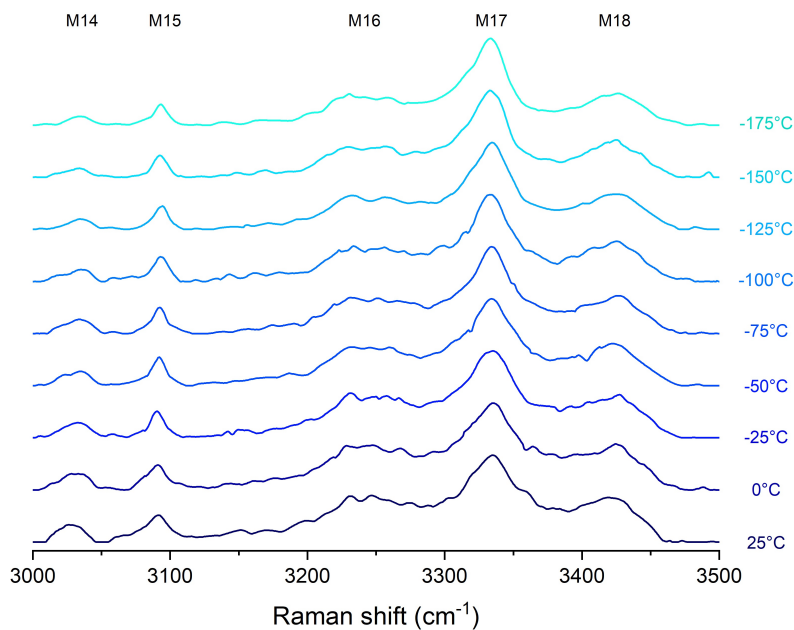
The experimental temperature-dependent Raman spectra of $MAPbBr_3$ and $FAPbBr_3$ are presented in Figure 4.21 and 4.22, respectively.

The molecular Raman modes of MA-based compounds appear around 800 cm^{-1} [65, 86] while for FA-based ones, the same start around 500 cm^{-1} [48, 103]. Since the PL signal of lead bromide perovskite compounds is weaker than iodide ones, it is possible to record a higher frequency range where the stretching modes are located: from 3000 to 3500 cm^{-1} for $FAPbBr_3$ and from 2800 to 3200 cm^{-1} for $MAPbBr_3$. According to the criterium of charge transfer interaction, these modes are more susceptible to present additional peaks when hydrogen bonds are involved. It is expected a higher probability of hydrogen bond formation in bromide compounds than in iodide ones due to the higher electronegativity of

Br^- compared to I^- (2.96 vs 2.66 on the Pauling scale) and the smaller ionic radius (1.96 vs 2.20 a.u.). Therefore, the absence of hydrogen bonds in bromide compounds implies the absence of them in iodide ones. Analogous to the attribution of Raman modes of MAI and FAI, we correlate the experimental peaks to the DFT calculated modes of the isolated molecules.



(a)



(b)

Figure 4.21: Raman spectra of $FAPbBr_3$ at different temperatures in a range from 25°C down to -175°C. Two energy regions are shown: (a) from 500 to 1800 cm^{-1} and (b) from 3000 to 3500 cm^{-1} .

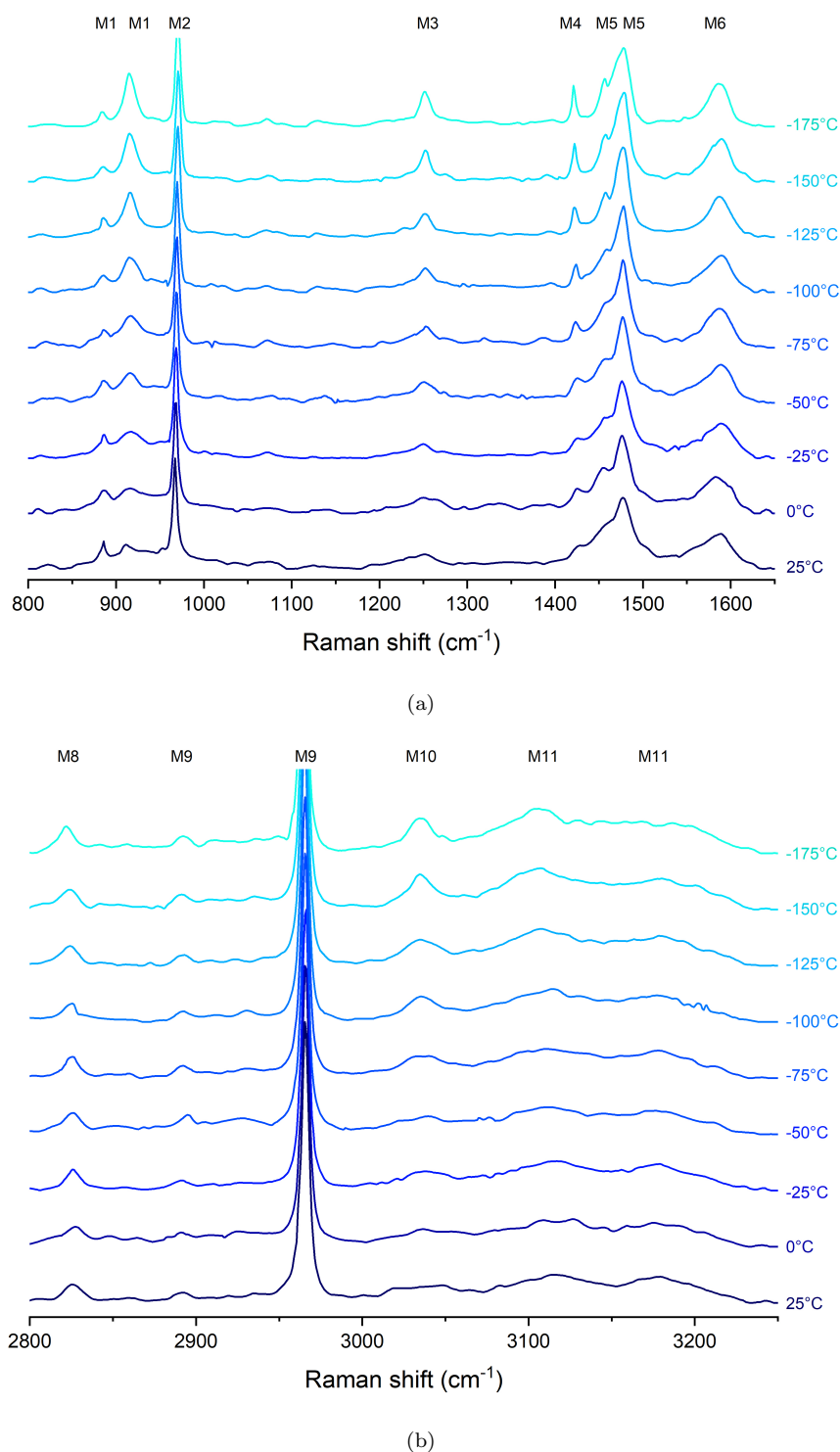


Figure 4.22: Raman spectra for $MAPbBr_3$ at different temperatures in a range from 25°C down to -175°C. Two energy regions are shown: (a) from 800 to 1700 cm^{-1} and (b) from 2800 to 3300 cm^{-1} .

In both compounds, the spectra present a shift lower than 4 cm^{-1} from 25°C to -175°C for all peaks. This magnitude represents an insignificant variation in the intensity of interaction with the octahedra.

$FAPbBr_3$ presents phase transitions from cubic to tetragonal at -11°C and to orthogonal at -135°C [108]. However, these are not noticeable in the spectrum. Peaks gradually broaden as a consequence of the lowering of symmetry that restricts the mode's activity. According to its tolerance factor of 1.008, the cubic form should be the best fit for the cation inside the inorganic cage. Tetragonal and orthorhombic structures compress the molecule, hindering its vibrational modes.

The visually appreciated apparition of M9 is not a mode activation but a consequence of the decrease of M10 width. It is clear that no additional modes appeared and, hence, we conclude the absence of hydrogen bonds in this compound. This fact agrees with our hypothesis of N-H...N bonds in FAI that discards the interaction with the halide.

$MAPbBr_3$ presents phase transitions from cubic to tetragonal at -36°C and to orthorhombic -123°C [65], which are also not shown in the spectra. In this case, the peaks sharpen with the lowering of temperature. According to the tolerance factor of 0.941, MA^+ has a higher free space inside the cell to vibrate. Therefore, the lowering of symmetric is not enough to restrict the molecular vibrations, as was the case of $FAPbBr_3$. The analogous case, broadening of molecular modes with the increase of temperature, was previously reported as a consequence of the unlocking of reorientation modes, which hinders the molecular vibrations [65]. The lack of additional modes implies the absence of hydrogen bonds.

4.3.1.3 Comparison at room temperature

The experimental Raman spectra of $FAPbX_3$ and $MAPbX_3$ are presented in Figure 4.23 and 4.24, respectively. Same as above, we attributed the modes in accordance with our calculations on isolated FA^+ and MA^+ species (see Tables 4.8 and 4.9).

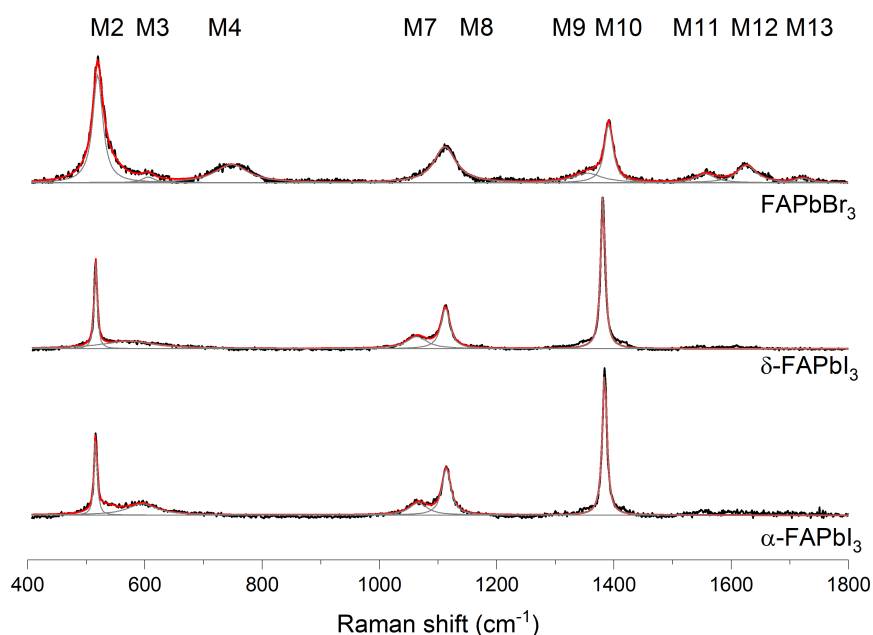


Figure 4.23: High frequency range of experimental Raman spectra of $FAPbI_3$ (α and δ) and $FAPbBr_3$ at RT.

Since $\alpha_i - FAPbI_3$ presents a high-intensity PL signal, it could not be measured with our excitation wavelengths (633 and 830 nm). Then, we compare the spectrum of α_δ and δ . The peaks of α_{rec} are taken from literature [103] and attributed according to our calculations.

Table 4.8: Experimental $FAPbI_3$ and $FAPbBr_3$ Raman modes and their attribution according to the DFT calculations of the isolated FA^+ molecule. The correlation has been started with the most intensive mode (*: DFT-548 cm^{-1} to Exp FAI (25°C)- 514 cm^{-1}). The frequency shifts appeared due two the following factors: i) presence of the PbI_6 framework and ii) temperature discarding approach of DFT calculations. $FAPbI_3$ is presented as: photoactive (degraded, α_δ [48] and α_{rec} [103]) and non-photoactive (degraded, δ).

Modes	Description of FA^+ Raman modes	Mode Frequency				
		DFT FA^+	$FAPbI_3$ (α_{rec})	$FAPbI_3$ (α_δ)	$FAPbI_3$ (δ)	$FAPbBr_3$
2	NH_2 sym. wagging	548*	516	516	516	520
3	$NH_2 - C - NH_2$ sym. bending	556	584	595	571	585
4	NH_2 asym. wagging	598	701	-	-	740
7	NH_2 scissoring + $C - H$ wagging	1079	-	1066	1064	-
8	NH_2 scissoring + $C - H$ stretching	1150	1112	1114	1112	1116
9	NH_2 rocking + $C - H$ wagging	1376	-	-	-	1353
10	NH_2 rocking + $C - H$ stretching	1384	1380	1384	1381	1391
11	$C - H$ bending + NH_2 scissoring	1610	1550	-	-	1558
12	NH_2 scissoring $C - H$ bending	1688	1613	-	-	1627
13	+ $C - N$ stretching + NH_2 scissoring	1762	-	-	-	1721

In the case of $FAPbX_3$, the position of the experimental peaks is close to the predicted one, facilitating the attribution. The Raman spectra $MAPbX_3$ are, on the contrary, more complicated than the analogous FA-compounds due to the double peak for the modes with E symmetry. This degeneration is shown by $\wedge$ in Fig 4.24. All the analyzed perovskites' Raman spectra can be completely attributed to the Raman modes of the respective isolated molecule. In general, Raman spectra of iodine compounds in the studied frequency range present fewer and sharper active modes than the bromide-containing counterpart. The difference in amplitude, better understood as a difference in width, is a consequence of the interaction with the halide. It is indeed wider for the most electronegative halide, which shows a stronger bond. However, the lack of an additional peak indicated that it is not a hydrogen bond and therefore, not directional.

We can extend this consideration to the Raman spectra found in the literature. On the one hand, we can compare iodide, bromide, and chloride compounds, and, on the other hand, we can study the stretching modes of the donor group. We expect that if there are

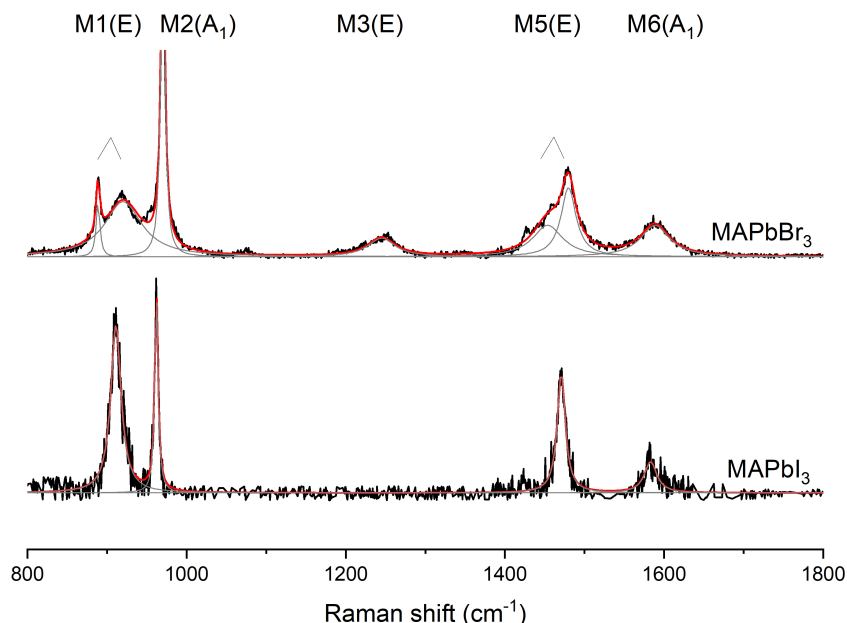


Figure 4.24: High frequency range of experimental Raman spectra of $MAPbI_3$ and $MAPbBr_3$ at RT.

Table 4.9: Experimental $MAPbI_3$ and $MAPbBr_3$ Raman modes attribution according to the DFT calculations of the isolated MA^+ molecule.

Modes	Description of MA^+ Raman modes	Sym. Group	Mode Frequency		
			DFT MA^+	$MAPbI_3$	$MAPbBr_3$
1	$C - N$ asym. bending	E	954, 966	910	889, 920
2	$C - N$ stretching	A_1	1004	962	969
3	$C - N$ asym. bending	E	1292, 1314	-	1244
4	CH_3 sym. bending	A_1	1469	-	-
5	CH_3 asym. bending	E	1492, 1501	1469	1455, 1478
6	NH_3 sym. bending	A_1	1582	1583	1589
7	NH_3 asym. bending	E	1680, 1694	-	-

hydrogen bonds, they would be shown preferentially in compounds with chloride and in the stretching modes, which are theoretically the last 4 peaks for $FAPbX_3$ and the last 3 for $MAPbX_3$. Raman spectra of the bending modes of $FAPbX_3$ are shown in Fig. 4.25 [103], while Raman spectra of stretching modes of $MAPbBr_3$ and $MAPbCl_3$ are shown in Fig. 4.26 [124].

For $FAPbX_3$, the pattern of the Raman spectra is invariant to the halide content. There is a reduction of the activity of out-of-plane vibrations ($>1000\text{ cm}^{-1}$) towards strongly electronegative halide [103], without an appearance of a secondary peak in any mode. This is the same case for the high-frequency modes of $MAPbBr_3$ and $MAPbCl_3$, corresponding to the stretching vibrations [124]. One of the peaks of the CH_3 asymmetric stretching mode is sharper than the adjacent modes, which is expected since the CH_3 group does not participate in the hydrogen bonding. Conversely, Xie et al [131] attribute a splitting of the stretching mode at 3059 cm^{-1} of $MAPbBr_3$ to hydrogen bonding, meanwhile, we justified

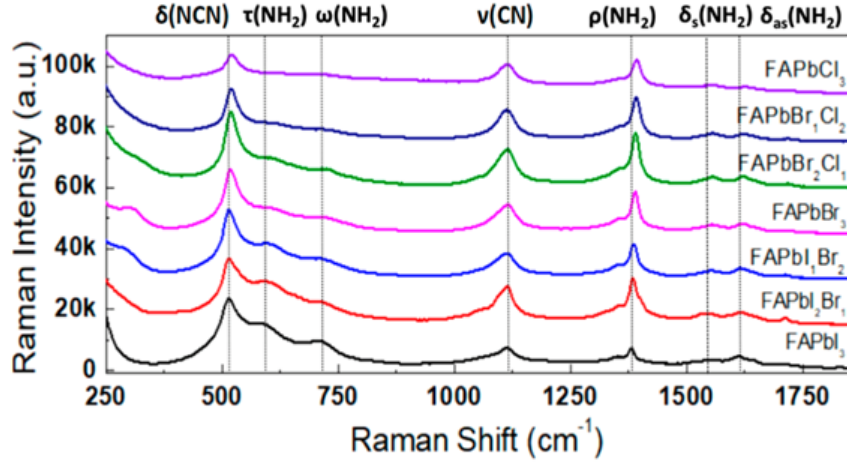


Figure 4.25: Raman spectra of bending modes of $FAPbX_3$, with X been combinations of I^- , Br^- and Cl^- [103]. License for reproduction in Annex.

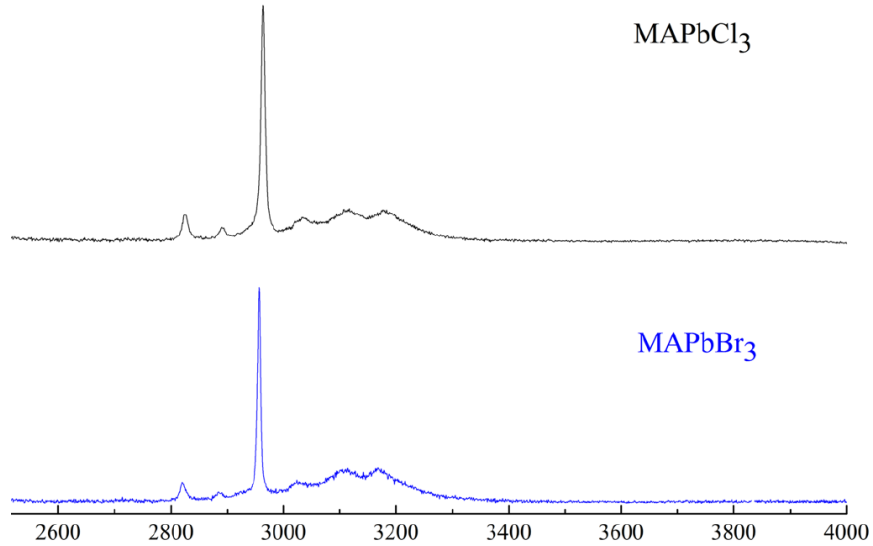


Figure 4.26: Raman spectra of stretching modes of $MAPbBr_3$ and $MAPbCl_3$ [124]. License for reproduction in Annex.

it to the double degenerated nature of the Raman mode. The high-frequency spectrum of $FAPbBr_3$ can also be completely attributed to the Raman modes of the isolated molecules [123].

In summary, there is no evidence of hydrogen bonding in the Raman spectra of lead halide perovskites. The shift of peaks with respect to a different halide can be attributed to another, non-directional interaction.

4.3.2 Discussion

Considering the lack of evidence in the hydrogen bonds in lead halide perovskites, we will explore the criteria of electronegativity of donor-acceptor and the minimum distance,

among other considerations. In literature, the existence of hydrogen bonds is generally verified by the presence of dipole moments and the magnitude of interatomic distances I...H [9, 100, 112, 129].

The experimental dipole moment of MA^+ in $MAPbI_3$ was obtained through temperature-dependent dielectric measurements [98]. The real and imaginary parts of the dielectric constant of $MAPbI_3$ were obtained from a dispersive polarizing millimeter-wave interferometer in a range from 50 to 150 GHz at ca. 200 to 300 K. At these temperatures, the perovskite structure is tetragonal I4/mcm. The values of the dielectric constant were fit from the Debye relaxation function to obtain the dipole moment, $\mu=0.854D$. However, several authors [9, 37, 109] refer to DFT calculations of the dipole moment for MA^+ in $MAPbI_3$ which gave a value of 2.25-2.29 D [34, 75]. The difference with the calculated value is due to the sensitive nature of the calculation methods, which is common for organic molecules. The value of the dipole depends on the refinement strategy, position of the hydrogen atoms, and overall, an over-parametrization of the models [99]. For example, calculations are in the gas phase with a polarizable continuum model with ethanol [34]. In the work of Madjet et al [74], MA^+ in the tetragonal perovskite has dipole moment values from 0.94D to 2.53D depending on the calculation method and partitioning scheme employed. Moreover, the calculation of partial charges can lead to ca. -3 to N, which is the opposite result from the theoretical analysis that expects N to accumulate the positive charge. The dipole moment of FA^+ has not been experimentally determined yet. Temperature-dependent dielectric measurements of $MAPbI_3$ and $FAPbI_3$ from 0 to 200K show that the dipole moment of FA^+ is smaller than MA^+ in the lead iodide perovskite [28]. This is also supported by DFT calculations, where the values are 2.2 D and 0.2 for MA^+ and FA^+ , respectively [34, 75]. If we consider this 10 times lower magnitude, that gives rise to expect almost zero dipole moment in FA^+ cation.

In terms of bonding energy, our results show no significant difference in the hydrogen bonding energy for the three different halides. The interaction is 0.10 to 0.15 eV stronger for the compounds based on MA^+ than those based on FA^+ , which coincides with the calculations of Svane et al. [114]. This may be a result of the larger dipole moment of MA^+ . Furthermore, this calculated hydrogen-bond energy is less than half the magnitude of perovskites with larger cations, which are proved to have hydrogen bonds by solid-state nuclear magnetic resonance spectroscopy. Then these calculations about bonding energy do not encourage the assignation of hydrogen bonds in lead halide perovskites with MA^+ and FA^+ as cations.

There are several methods to determine the Van der Waals radius of an element, which give different results. It depends on the chemical environment surrounding the element. In a general case, we can take a first approximation from Bondi, $r_{WdV} = 3.18\text{\AA}$ [11]. The interatomic distances from calculations depend strongly on the modelled crystalline structure. For $MAPbI_3$, it goes from 2.49-2.67 $\text{\AA}$ and 2.82 $\text{\AA}$ in orthorhombic, varying to equivalent 2.5 $\text{\AA}$ for tetragonal structures [100]. These values can also reach 3.5 $\text{\AA}$ and angles from 0 to 140° under different calculation methods [4]. Varying the halide leads to calculated distances of 2.45 $\text{\AA}$ for Br and 2.3 $\text{\AA}$ for Cl [89]. Experimentally, the NH...I bonding distances of $FAPbI_3$ are deduced from the atomic positions given by neutron powder diffraction of recovered crystals. These are 2.992 and 2.770 $\text{\AA}$ for the different

hydrogens involved. The C-H group has been determined to be not bonded at 3.572 Å [129]. The uncertainty of determination makes that this criterium cannot stand on its own. In combination with the neglectable dipole moment and the lack of evidence in the Raman spectrum, we conclude that these lead halide perovskites do not present hydrogen bonds.

4.3.3 Summary

In this work, we proved the absence of hydrogen bonding in lead halide perovskites through the analysis of the Raman spectra. For this, we employed a criterion of an additional peak in the spectrum compared to the respective isolated molecule, which is related to the charge transfer proper of this kind of bond. The first step was the characterization of the isolated molecules through DFT calculations since data of MA^+ was missing and additional information of FA^+ was needed. Our results showed small differences ($< 10\%$) with the Raman data available in the literature. Here we identified the hydrogen atoms involved in the Raman modes of FA^+ . To prove the method, we analyze temperature-dependent Raman spectra of FAI and MAI salts. We confirmed the presence of hydrogen bonds of FAI at low temperatures (-200°C), determined a temperature range for the bond formation, and suggest that the bond is N-H...N, which is normal in amines. Moreover, the H atoms involved are the pair closer to C-H. In MAI, the bond formation likely occurs around -175°C , however, we do not have enough proof to catalog it as hydrogen bonding. Finally, the Raman spectra of $MAPbI_3$, $MAPbBr_3$, $FAPbI_3(\alpha \text{ and } \delta)$, and $FAPbBr_3$ can be attributed to the Raman modes of the respective isolated molecules, indicating that the bonding that shifts the spectra is not directional by nature. This implies that the structural stability of perovskites compounds, among other phenomena, is not caused by directional binding but is most likely to structural factors such as stresses. Further analysis of this conclusion may lead to a better understanding of the material and better design of this material for optoelectronic applications.

4.4 Stability of mixed compounds

Lead halide perovskite semiconductors that provide record efficiencies of solar cells usually have mixed compositions doped in A- and X-sites to enhance phase stability. The cubic form of $FAPbI_3$ reveals excellent optoelectronic properties but transforms at RT into a hexagonal structure that does not effectively absorb visible light. This metastable form and the mechanism of its stabilization by Cs^+ and Br^- incorporation are poorly characterized and insufficiently understood.

In this chapter, we investigate the effect of the incorporation of Cs^+ and Br^- into $FAPbI_3$ using micro-Raman spectroscopy and identify the origin of the different vibrational modes with the support of DFT calculations. The single crystal was synthesized and characterized as described in Chapter 3.1 and 3.3. We compare the mixed compounds $Cs_{0.1}FA_{0.9}PbI_3$ and $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$ with the related pure compounds: $FAPbI_3$, $FAPbBr_3$ and $CsPbBr_3$. From these last ones, only Zone I and II of $FAPbBr_3$ have not been determined in the literature. We attributed the experimental Raman modes for these Zones of $FAPbBr_3$ through DFT calculations Chapter 4.1. We analyze the impact of Cs^+ and Br^- incorporation into $FAPbI_3$ in Chapter 4.2, using the quantification of Raman modes and Raman shifts. In particular, we focus on the identification of vibrational modes in the low-frequency region ($< 500 cm^{-1}$). A compositional cross-check is performed: single-crystalline $FAPbI_3$ and $FAPbBr_3$ are compared to identify the sublattice PbX_6 modes and FA^+ movements. The effect of the incorporation of these atoms is discussed in Chapter 4.3. Finally, we summarize the findings in Chapter 4.4.

Our results show that the incorporation of Cs^+ and Br^- leads to the coupling of the displacement of the A-site components and weakens the bonds between FA^+ and the PbX_6 octahedra. We suggest that the enhancement of $\alpha - FAPbI_3$ stability can be a product of the release of tensile stresses in the Pb-X bond, which is reflected in a red-shift of the low-frequency region of the Raman spectrum ($< 200 cm^{-1}$). Comparing $FAPbBr_3$ with $CsPbBr_3$ enables the identification of Br^- related vibrational modes and to differentiate between FA^+ and Cs^+ cations. A complex effect of the partial cation and anion substitutions is observed in relatively stable $Cs_{0.1}FA_{0.9}PbI_3$ and $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$ compositions.

4.4.1 Raman spectrum of $FAPbBr_3$

Theoretical Raman modes

Raman spectrum of $FAPbBr_3$ has been experimentally characterized from 60 to $3500 cm^{-1}$ [123]. Despite it, only high-frequency modes (Zone III) have been attributed according to the calculated Raman modes of the isolated FA^+ [60]. Here, we implement the model of Chapter 4.1 to obtain the Raman modes of Zone I and II of $FAPbBr_3$ and compare it with the calculated modes of $FAPbI_3$, as presented in Fig. 4.1.

The Raman modes of **Zone I** of $FAPbBr_3$, show octahedral twist modes at 30 and $31 cm^{-1}$ and octahedral distortion at 34, 44 and $63 cm^{-1}$. This blue-shift of ca. $15 cm^{-1}$ compared

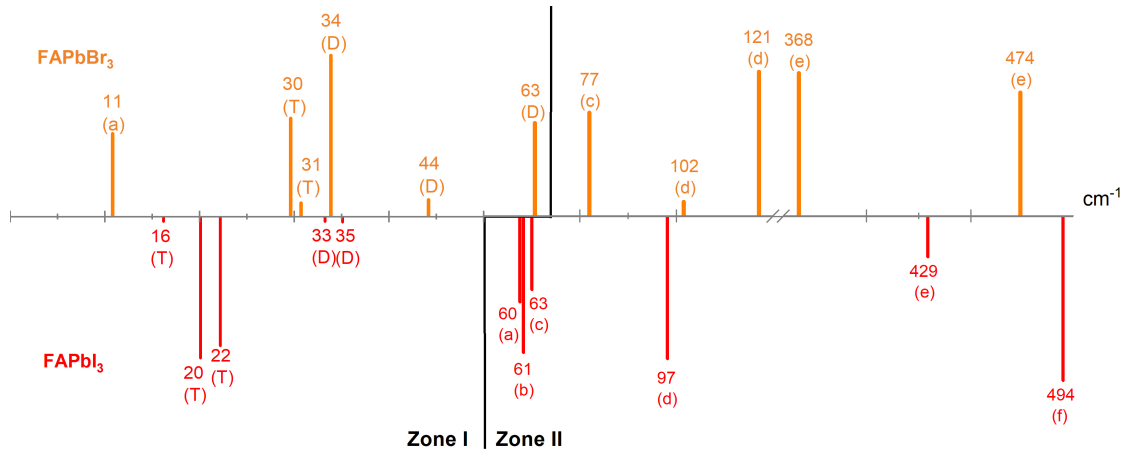


Figure 4.27: Comparison of DFT calculated Raman spectra for the cubic $FAPbBr_3$ (orange) and $FAPbI_3$ (red). Raman modes are identified according to the vibrations of Zone I: T) Octahedral twist, D) Octahedral distortion; and Zone II: a) in-plane rotation around the center of mass, b) in-plane rotation around corner hydrogen, c) out-of-plane rotation around the N-N axis, d) FA^+ translation along with the C-H bond, e) $H_2N - C - NH_2$ asymmetric out-of-plane bending and f) $H_2N - C - NH_2$ symmetric out-of-plane bending. The black line divides Zone I and Zone II of the respective perovskites.

to $FAPbI_3$ is expected due to the higher strength of the Pb-Br bond compared to Pb-I (0.66 vs 0.33 on the Pauling scale) as well as due to the smaller atomic mass of Br compared to I (79.9 u. vs 126.9 u.). As briefly described in Chapter 2.1.5, the Raman frequency can be simplistic understood as the harmonic oscillator model of a diatomic molecule, $\omega = \sqrt{k/m}$ [128]. As a parallel to a mechanical system, "m" represents the reduced mass, and "k", the spring constant or, in this case, the strength of the chemical bond.

In **Zone II**, $FAPbBr_3$ reveals the same modes of $FAPbI_3$ with the exception of mode (b) at 11, 77, 102/121, 368 and 474 cm^{-1} , as presented in Fig. 4.27. The halide substitution is not reflected in a unidirectional blue shift as in Zone I. In the following, we compare the frequency of each mode ($FAPbBr_3/FAPbI_3$) and present a possible justification

- (a) (11/60): The rotation plane is parallel to the crystallographic plane in $FAPbBr_3$ but slightly tilted in the case of $FAPbI_3$ due to the larger free space of the last one.
- (b) (-/61): The smaller size of the unit cell in $FAPbBr_3$ makes unfavorable such a notable shift of FA^+ .
- (c) (77/63): Expected blue-shift.
- (d) (102/97): Expected blue-shift.
- (e) (368/429): in $FAPbI_3$, the mode is governed by displacements of H atoms bonded to N. On the contrary, in $FAPbBr_3$ these H atoms remain almost static while Br^- ions displace. This is a consequence of the weaker interaction $H \leftrightarrow I$ compared to $H \leftrightarrow Br$.
- (f) (474/494) The larger free space in $FAPbI_3$ allows weaker interaction with the inorganic frame.

Experimental Raman modes

Peaks of the experimental Raman modes of $FAPbBr_3$ are attributed according to the DFT calculations presented above. Fig. 4.28 presents the Raman spectrum and the fitting curves.

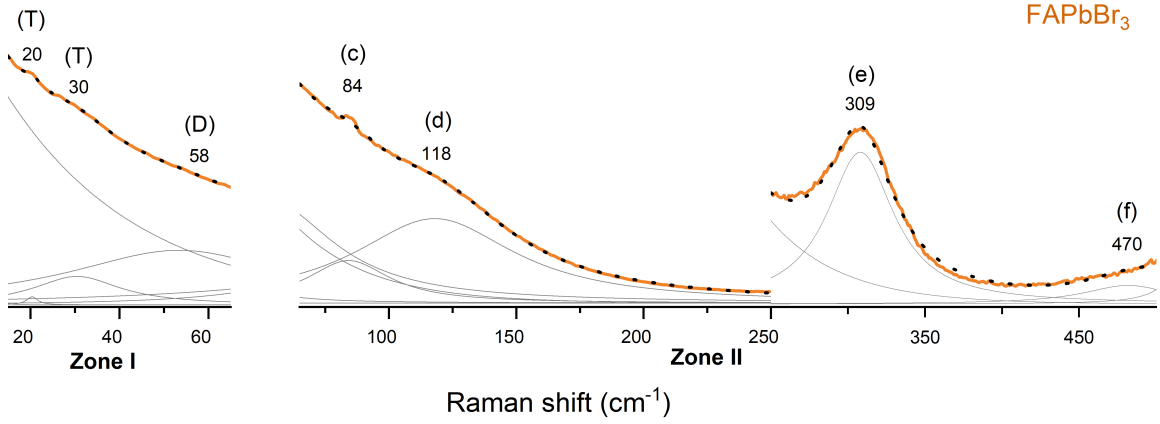


Figure 4.28: Attribution of Raman modes of Zones I and II of the experimental spectrum of $FAPbBr_3$. The notation is based on the DFT calculations previously presented. The orange line represents the measured spectrum, black dashed lines are the fitted curve and gray lines indicate fitted peaks with Lorentzian line shape.

It is remarkable to correlate this spectrum with the one of $\alpha_{HT} - FAPbI_3$ in a range from 15 to 200 cm^{-1} . Both spectra present unnoticeable peaks at eye level and, hence, we consider both structures as cubic $Pm\bar{3}m$ with inactive Raman modes. The difference with the spectrum of $FAPbI_3$ at RT is likely due to the stronger Pb-Br bonds and closer-to-unity Goldschmidt Tolerance Factor (GTF). The smaller ionic radius ensures a better fit of FA^+ in the cubic cell.

We analyze the mathematical construction of the spectrum. However, the overlapping of broad Lorentzian curves may not correspond to Raman modes and the peak positions have a high degree of uncertainty. The following attribution aims only for comparison purposes with mixed compounds.

In **Zone I** of the experimental spectrum, three peaks are identified. Two peaks, at 20 and 30 cm^{-1} may be attributed to the octahedral twist mode, while the peak at 58 cm^{-1} to the distortion mode. Considering a cubic lattice, only one peak could represent each mode of the O_h symmetry. Thus, we select the peak at 30 cm^{-1} as a twist due to its higher activity.

Zone II has one unmistakable peak at 309 cm^{-1} which is attributed to mode (e), $H_2N - C - NH_2$ asymmetric out of plane bending. The red-shift of this mode compared to the calculated one to a higher sensitivity of the lattice to out-of-plane moves.

Four additional peaks can be identified, which coincide with the Raman modes predicted for this zone. Then, the experimental Raman modes are theorized as follows. Mode (c) at 84 cm^{-1} , (d) at 118, (e) at 309 cm^{-1} and (f) at 470 cm^{-1} . The red-shift of mode (e) compared to the calculated ones may be related to weaker interaction than the predicted one.

4.4.2 Effect of the partial Cs^+ and Br^- substitutions

At this point, the calculated and experimental Raman modes of $FAPbI_3$ and $FAPbBr_3$ are determined. Zone I and II are discussed in Chapters 4.1.3 and 4.4.1, respectively, while Zone III was attributed from the calculated modes of the isolated FA^+ in Chapter 4.2. Thus, we focus on the effect of partial substitution of FA^+ by Cs^+ and I^- by Br^- on the Raman spectrum of $FAPbI_3$ and the stabilization of the cubic form. The Raman spectra of mixed compounds, $Cs_{0.1}FA_{0.9}FAPbI_3$ and $Cs_{0.1}FA_{0.9}FAPbI_{2.6}Br_{0.4}$, are presented in Fig. 4.29. For clarity, exclusively Raman modes are indicated by Lorentzian peaks.

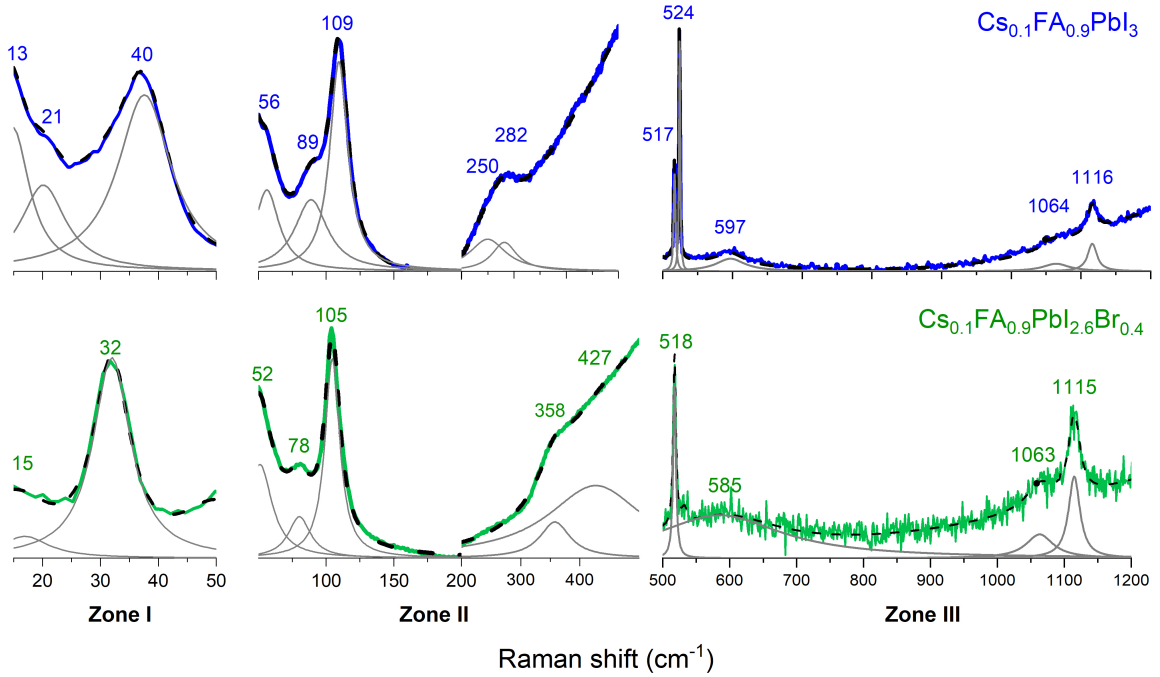


Figure 4.29: Raman spectra of $Cs_{0.1}FA_{0.9}FAPbI_3$ and $Cs_{0.1}FA_{0.9}FAPbI_{2.6}Br_{0.4}$ single crystals at RT with an excitation wavelength of $\lambda = 633nm$, divided into three zones according to the vibration source. Color lines represent measured spectra, black dashed lines are fits to the spectra, and gray lines indicate fitted peaks with Lorentzian line shape.

From an initial inspection, the Raman spectra of the mixed compound can be completely attributed from 10 to 200 cm^{-1} by the Raman modes of $\alpha_i - FAPbI_3$ and from 200 to 500 cm^{-1} by the modes of $FAPbBr_3$. Experimental Raman modes of Zone III are extracted from the $\alpha_\delta - FAPbI_3$. As we explicit in Chapter 4.2, these modes are indistinguishable from the α_i phase, with the exemption of a shift with a mean value of 4 cm^{-1} .

For a better comparison of the Raman spectra, we previously performed XRD and PL measurements of $FAPbI_3$ and the chosen mixed compounds.

Due to the similarity of the XRD measurements presented in Fig. 4.30, we calculate the lattice parameter by fitting the all the patterns with a cubic $Pm\bar{3}m$ symmetry. As presented in Chapter 4.2, XRD is not sensible to the cation organization and, thus, the fitting with this symmetry represents the experimental patterns quite well. As seen in Fig. 4.30b, the (100) diffraction maximum shifts only when Cs^+ and Br^- are incorporated. The corresponding lattice constants are 6.357 Å for $FAPbI_3$ and $Cs_{0.1}FA_{0.9}PbI_3$, and 6.293 Å

Table 4.10: Classification of Raman peaks of FA-based compounds. Raman modes of Zone I and II are attributed according to DFT calculations of $FAPbI_3$ and $FAPbBr_3$. Modes in III correspond to DFT calculations of isolated FA^+ . Notation correlates to Chapter 4.1.3, 4.3 and 4.4. Modes frequencies labelled “#” indicate broad and/or weak shoulder-like peaks without sharp peak-maximum. Experimental Raman modes of $FAPbI_3$ below 200 cm^{-1} correspond to the α_i -phase, while above to α_δ .

Mode	Description	$FAPbI_3$	$Cs_{0.1}FA_{0.9}PbI_3$	$Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$	$FAPbBr_3$
T	Octahedra twist		13#, 21#	15	20#
D	Octahedra distortion	43	40	32	58#
1	in-plane rotation	63#	52#	50#	
2	out-of-plane rotation around N-N axis	96#	89#	78#	84#
3	FA^+ Translation	114	109	105	118#
4	out-of-plane sym. bending $HN - C - NH$		250	358	309
5	out-of-plane asym. bending $H_2N - C - NH_2$		282#	427#	470#
1	NH_2 sym. wagging	516	517, 524	518	522
2	$H_2N - C - NH_2$ sym. bending	597	597	585	567
3	NH_2 asym. wagging				746
4	NH_2 scissoring + $C - H$ wagging	1062	1064#	1063#	
5	NH_2 scissoring + $C - H$ stretching	1114	1115	1116	1112

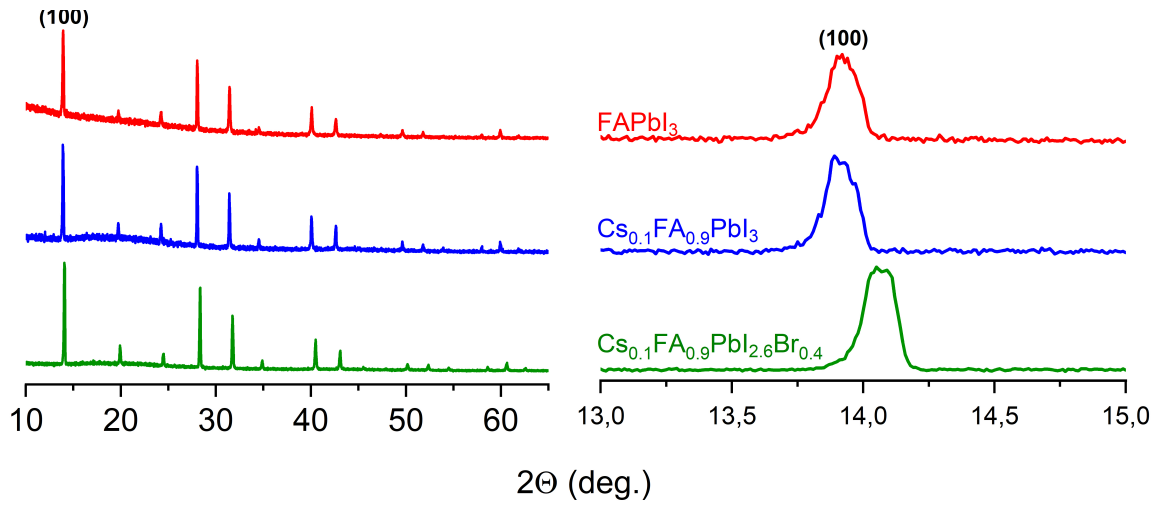


Figure 4.30: Powder XRD patterns of as-prepared $FAPbI_3$ -based perovskites: (left) wide range and (right) selected 2θ area around (100) reflection in a cubic $Pm\bar{3}m$ system. Lattice constants were calculated on the basis of Rietveld refinement over the whole measured 2θ range.

for $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$. Our SC XRD showed a similar result for $FAPbI_3$ at RT: $6.364\text{ \AA}$. Considering the lattice constant of cubic $CsPbI_3$ ($6.242\text{ \AA}$ [3]), a continuity of the phase-structure of $FAPbI_3$ can be expected with the incorporation of Cs^+ . On the contrary, the

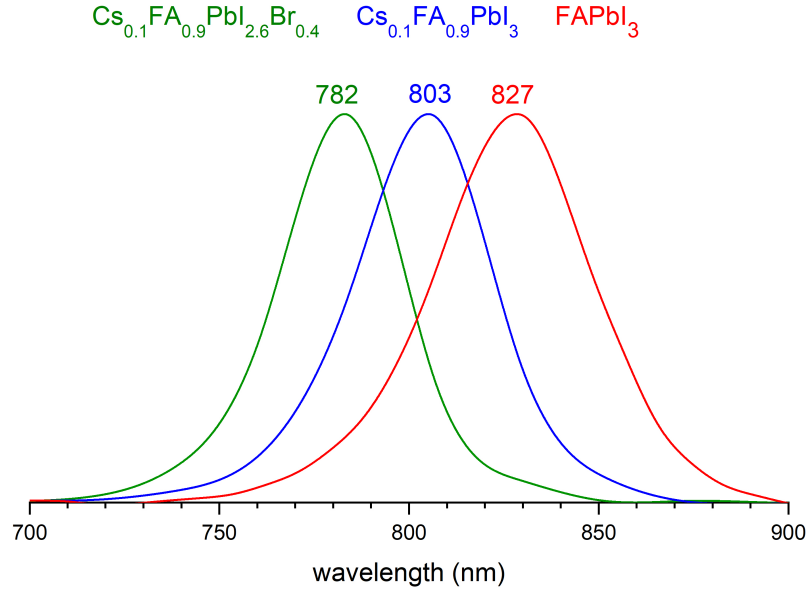


Figure 4.31: Normalized PL signals (spline smoothed curve) of $FAPbI_3$, $Cs_{0.1}FA_{0.9}PbI_3$ and for $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$ measured with an excitation source of 633 nm

partial substitution of I^- by Br^- results in a decrease in the lattice constant due to the smaller size and more electronegative character of the incorporated halide.

The PL signal of Fig. 4.31 shows a singular peak for each composition. This means that secondary phases such as separated Cs-rich or Br-rich zones are absent and we can assume a homogeneous distribution of Cs^+ and Br^- in the mixed compositions. We also expect no symmetry change with respect to the cubic $FAPbI_3$. Additionally, there is a shift of 24 and 21 nm from $FAPbI_3$ with respect to the inclusion of Cs^+ and both Cs^+ and Br^- , respectively. Since according to XRD there is no variation in the lattice parameter with the Cs^+ partial substitution, the shift indicates a change in the Pb-I angle. Therefore, we expect that Cs^+ contributes to the lattice distortion of $FAPbI_3$.

After determining the lattice size and composition of the SC, we compare the spectra of the mixed compounds with $FAPbI_3$, $FAPbBr_3$, and $CsPbBr_3$ in their coinciding frequency range.

Effect of Cs^+ incorporation

We analyze first the Raman spectrum of $Cs_{0.1}FA_{0.9}PbI_3$. Within the range from 15 to 200 cm^{-1} , the spectrum shows a red-shift with a magnitude of ca. 4 cm^{-1} respect to $FAPbI_3$, while from 200 to 500 cm^{-1} , the shift is larger than 100 cm^{-1} compared to $FAPbBr_3$.

In **Zone I**, the appearance of two peaks at 13 and 21 cm^{-1} for the twist mode implies a lower symmetry than the cubic one. Considering that the lattice size is constant with the incorporation of Cs^+ cation, the red-shift of the distortion mode at 40 cm^{-1} indicates a variation of the Pb-I bond angle. Indeed, an increase in distortion as expected. Cs^+ has a considerably smaller ionic radius (1.81 vs 2.53 Å), is heavier and more electronically spherical, thus, it should have notably stronger ionic interaction with the PbI_6 framework than the FA^+ molecules.

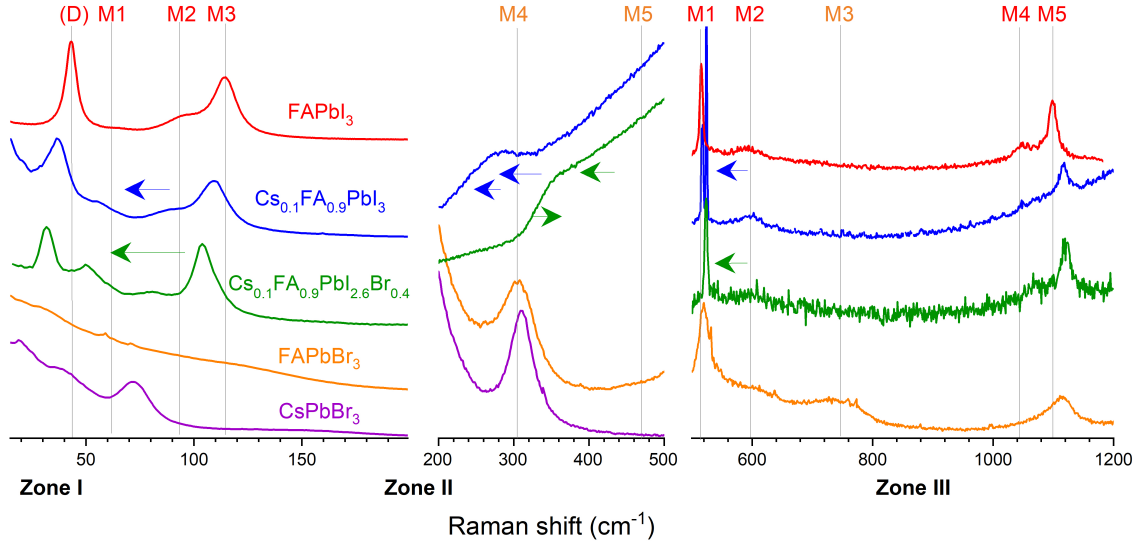


Figure 4.32: Raman spectra of $Cs_{0.1}FA_{0.9}PbI_3$ and $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$ compared to $FAPbI_3$, $FAPbBr_3$ and $CsPbBr_3$. Modes of the same vibrational origin in the different LHPs are compared with experimental modes of $FAPbI_3$ and the shift is denoted by adjacent arrows. In the range 200 to 500 cm^{-1} , $FAPbI_3$ does not present modes and the comparison is made with $FAPbBr_3$ Raman modes. Color of the mode attribution corresponds to the color of the compared compound.

For the analysis of **Zone II**, we consider the atomic displacement of Cs^+ from the A-position in the $FAPbI_3$ matrix. To this end, we compared $Cs_{0.1}FA_{0.9}PbI_3$ with $CsPbBr_3$. In this last, the Cs^+ trajectories are known[132]: the cations move 0.85 Å in a head-to-head motion, stabilized by a cooperative motion of Br^- ions. In another word, two cations of adjacent unit cells move towards their shared side, meanwhile the Br^- ions located at that side simultaneously move away from the unit cell due to Pauli repulsion forces. This is schematized in Fig. 4.33 and represented in the Raman spectrum by the peak at 72 cm^{-1} . Summarizing, we have the translation of Cs^+ at 72 cm^{-1} and FA^+ at 114 cm^{-1} . The peak resulting from the combination of both is linearly distributed between both of them: exactly at 10% of the difference from $FAPbI_3$. This fact, together with the homogeneous distribution of Cs^+ , indicates coordination of the cation translation.

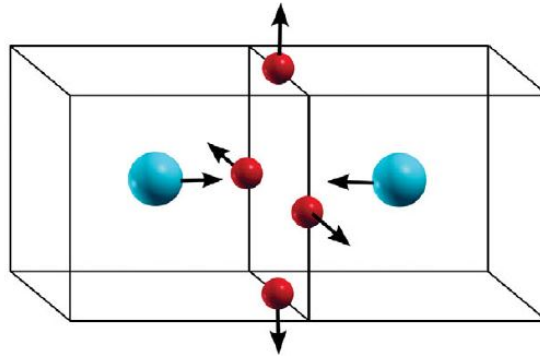


Figure 4.33: Schematic representation of the Raman mode of $CsPbBr_3$ head-to-head motion of Cs^+ and cooperative expansion of Br^- ions. Reproduced from [132].

In the range from 200 to 500 cm^{-1} , the spectrum presents a bump that can be decomposed

into two peaks at 250 cm^{-1} and 282 cm^{-1} . In this range, there are only two modes calculated for $FAPbX_3$ compounds: sym. (e) and asym. (f) $NH_2 - C - NH_2$ out-of-plane bending. These modes appear in $FAPbBr_3$ at 309 and 470 cm^{-1} , respectively.

The Raman spectrum of $CsPbBr_3$ presents a peak at 312 cm^{-1} , which is related to second-order-phonon mode of Cs^+ translation [18]. This may influence the FA^+ -bending via variations of the internal electric field, resulting in larger displacements of lead and halide in this vibration. In turn, it decreases the frequency of the modes.

Zone III of the Raman spectrum of $Cs_{0.1}FA_{0.9}PbI_3$ presents peaks at frequencies close to the Raman modes of $FAPbI_3$, slightly blue-shifted by 2 cm^{-1} maximum. An exception to this is the high-intensity peak at 524 cm^{-1} in the mixed compound. This peak could be considered a split of the Raman mode at 526 cm^{-1} in $FAPbI_3$, NH_2 sym. wagging. As concluded in Chapter 4.3, FA^+ does not form hydrogen bonds with I^- . Then, the additional peak should be related to a different electric charge affecting the molecular cations. This could be either the distortion of the inorganic lattice as previously mentioned in Zone I or the effect of Pauli repulsion on the molecules adjacent to Cs^+ atoms. The reason why only this mode is affected is due to it being the sole active mode of $FAPbI_3$ in Zone III that involves out-of-plane displacements, as seen in Chapter 4.3.

Effect of Cs^+ and Br^- incorporation

The effect of Br^- incorporation into $Cs_{0.1}FA_{0.9}PbI_3$ is demonstrated as a red-shift in the spectrum for frequencies lower than 200 cm^{-1} . The most prominent shift has a magnitude of 12 cm^{-1} and is related to the octahedral distortion. This is counterintuitive since $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$ has shorter Pb-X bonds and thus, should present higher frequencies. This is extracted from the smaller cell size calculated from the XRD patterns and the lower wavelengths of the PL signal and is justified by the lower atomic mass and higher electronegative of Br^- ions compared to I^- . This redshift that accompanies the substitution of I^- by Br^- is also present in $CsPbBr_3$ as compared to $CsPbI_3$. For frequencies below 200 cm^{-1} , the most prominent peak of the octahedral distortion mode is located at 55 cm^{-1} for I^- and 40 for Br^- , while the analogous peak of the cation translation mode is present at 108 and 73 , respectively (see Chapter 2.1.5). The compactness of the $CsPbBr_3$ structure is higher than the one of $CsPbI_3$, as suggested by a GTF closer to 1 (0.974 vs 0.836 , respectively). Therefore, we suggest an effect of the strength release of the Pb-X bonds as in both cases redshift is accompanied by an increase of GTF(see Table 4.11).

Table 4.11: Relevant Goldschmidt tolerance factors (GTFs) [36, 66]

Material	GTF
$FAPbI_3$	0.987
$Cs_{0.1}FA_{0.9}PbI_3$	0.972
$Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$	0.974
$FAPbBr_3$	1.008
$CsPbI_3$	0.836
$CsPbBr_3$	0.974

In **Zone I**, the disappearance of the second peak of the "Octahedra twist" mode at 21 cm^{-1} of $Cs_{0.1}FA_{0.9}PbI_3$ suggests a cubic lattice. The red-shift of the octahedral modes respect

indicates a smaller cell size, which coincides with the XRD results. The transition to cubic can be explained as the interaction of two opposite effects: additional stresses in the PbX_6 structure caused by the incorporation of Cs^+ and stress release by the incorporation of Br^- .

The peaks of **Zone II** below 200 cm^{-1} are red-shifted as previously discussed. Between 200 and 500 cm^{-1} , the Raman modes are blue-shift as expected from the addition of an halide with stronger electronegativity: shoulder peaks at 250 and 282 cm^{-1} in $Cs_{0.1}FA_{0.9}PbI_3$ shift to 358 and 427 cm^{-1} in $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$. The inorganic frame is more rigid with the incorporation of Br^- and has a less intense response to the molecular reorganization modes of this zone.

The Raman modes of the **Zone III** of $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$ present frequencies close to the modes of $Cs_{0.1}FA_{0.9}PbI_3$, however, mode M1 of this zone is not split. The absence of splitting can be explained by the less distorted structure, as presented above. The incorporation of Br^- does not active the Raman mode M3 present in $FAPbBr_3$ at 746 cm^{-1} , which is related to the combined vibration of NH_2 asym. wagging and scissoring. The activation of different modes depending on the halide content is likely a consequence of the lattice size.

The enhanced stability of $Cs_{0.1}FA_{0.9}PbI_3$ and $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$ respect to $FAPbI_3$ can be explained by an increase of the I_{M2}/I_{M3} ratio, 1.11 vs 0.22, as presented in Chapter 4.2.1. In the first compound, the restriction of the volumetric rotation of the molecular cation can be attributed to the increased distortion produced by the cation's coordinated vibration. The structural stability of these compounds lasts ca. 7 weeks, finally degrading into PbI_2 . The second compound has higher stability, maintaining its perovskite organization for more than 10 weeks. The I_{M2}/I_{M3} ratio corresponds with the enhanced stability, increasing to 2.67. This is a consequence of the more rigid inorganic frame and more compact unit cell that hinders the molecular rotation. Therefore, we support the theory of the volumetric rotation of the FA^+ molecule as the main factor in the structural instability of $FAPbI_3$.

4.4.3 Summary

We reported experimental spectra of mixed compositions based on $FAPbI_3$: $Cs_{0.1}FA_{0.9}PbI_3$ and $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$. The attribution of Raman modes was made by comparison with pure perovskite compounds: $FAPbBr_3$, $FAPbI_3$, and $CsPbBr_3$. For the first one, we presented the experimental spectrum and correlated it with the calculated modes by DFT.

From 10 to 200 cm^{-1} , the mixed compounds present red-shifted peaks compared to $FAPbI_3$. From 200 to 500 cm^{-1} , the spectra of the mixed show two peaks, as happens in $FAPbBr_3$. At last, from 500 cm^{-1} , the spectra is blue shifted compared to $FAPbI_3$. Here, $Cs_{0.1}FA_{0.9}PbI_3$ has a split mode around 520 cm^{-1} .

The incorporation of Cs^+ into $FAPbI_3$ increases the distortion, maintaining the lattice cell size, and coordinates the cation translation. The incorporation of both Cs^+ and Br^+ keeps the cubic organization and increases the compactness of the cell and the rigidity of the inorganic frame. In both compounds, the incorporation of an additional element restricts the rotation of FA^+ around the N-N axis, resulting in enhanced structural stability.

4.5 Application in thin-film optoelectronic devices

From the analyses made in the previous chapters, it can be concluded that the structural instability of $FAPbI_3$ is a result of the rotation of the FA^+ molecule around the N-N axis that stresses the unit cell. This movement can be suppressed by the presence of defects and contained by increasing the size of the unit cell.

In the first case, the defect can be considered as a point defect, such as substitutions of elements in the primitive cell by mixing the composition of the perovskite, or complex defects such as the secondary phases product of the partial transformation of the alpha phase into δ and PbI_2 .

The second case refers to the available free space inside the unit cell. From our temperature-dependent analyses, we estimated a phase transition temperature in the range from 100°C to 110°C. Above this temperature, the halide displacement and the unit cell size are sufficient for the FA^+ molecule to rotate without interfering with the surrounding octahedra. Also, each state of the α -phase (α_i , α_δ , α_{rec}) lasts a different amount of time in its cubic phase because of the combined effect of cell size, deduced from the Raman spectra, and the presence of secondary phases. Several experimental characterizations of $FAPbI_3$ rely on the annealing of the material posterior to the degradation into the δ -phase [45, 129]. Additionally, it is known that the density of the defects influences the performance of perovskites as light-absorbers when used in optoelectronic devices. Then, the questions are:

1. What is the impact of the annealing temperature on the structure of $FAPbI_3$?
2. How sensitive is the performance of an optoelectronic device regarding the lattice size and defectiveness of the film?

In chapter 4.5.1, it will be studied the effect of the annealing temperature in the first stage of preparing a $FAPbI_3$ thin film, just after deposition. The annealing temperature of the second stage, to recover the degraded state, is kept constant. In Chapter 4.5.2, the sensitivity of a solar cell performance with respect to the lattice through the variation of the bandgap and defect density will be studied via simulations of a n-i-p device structure.

4.5.1 Impact of the annealing temperature in thin films

Thin films were deposited in a two-step spin-coating process [See Methods 3]. First, we prove that the structure of thin films and SC are the same. The chosen SCs for this comparison were nucleated at 90°C, from where the temperature increases 5°C each 30 min, and kept for 3 h at 120°C to grow. Thin films are annealed at the same temperature of SC growth, 120°C. The experimental patterns present in Fig. 4.34 are smoothed to decrease noise and normalized. Differences in the intensity of peaks between samples are due to different predominant dispositions measured by XRD.

There are no major differences between the experimental XRD patterns of SC and thin film, therefore, the material presents the same symmetry. α_i was previously proposed to

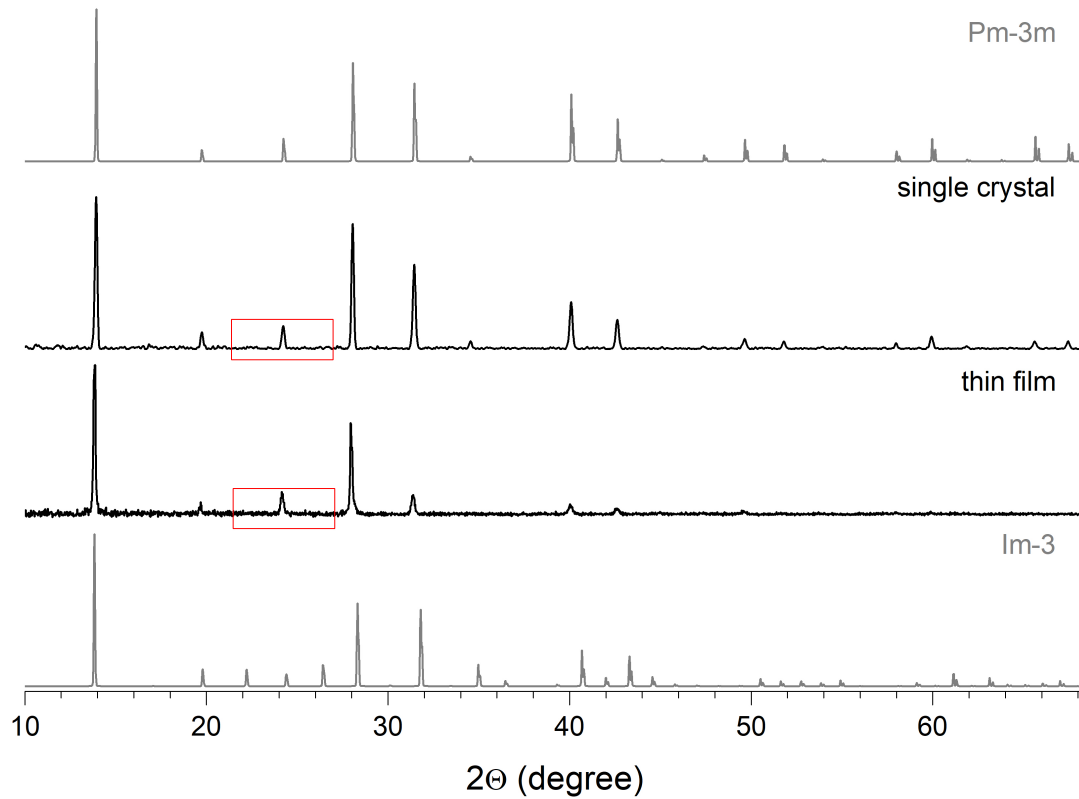


Figure 4.34: Comparison of XRD patterns of α_i - $FAPbI_3$ SCs grown at 120°C and thin films annealed at 120°C.

possess an $Im\bar{3}$ symmetry, however, there are no diffraction maxima, characteristic of this symmetry. For instance, the expected peaks at 22.5° and 26.5° are absent, as shown in the red area in Fig. 4.34. As it was stated before, the deviation of the proposed crystal structure from the perfect cubic symmetry is related to the displacement of I ions, which are large and possess a dispersed electron cloud. On average, the positions of these ions correspond to the expected from the primitive cubic symmetry and so are perceived by XRD. As Raman spectroscopy can detect this vibration due to the frequency of the emitted photons, the analyzed structure is different. In conclusion, thin films patterns are fit with the $Pm\bar{3}m$ space group.

In the following, the XRD patterns of the three states: as-deposited, degraded, and thermally recovered are presented in Figs. 4.35, 4.36 and 4.37. The corresponding Pawley analysis data are shown in Table 4.12.

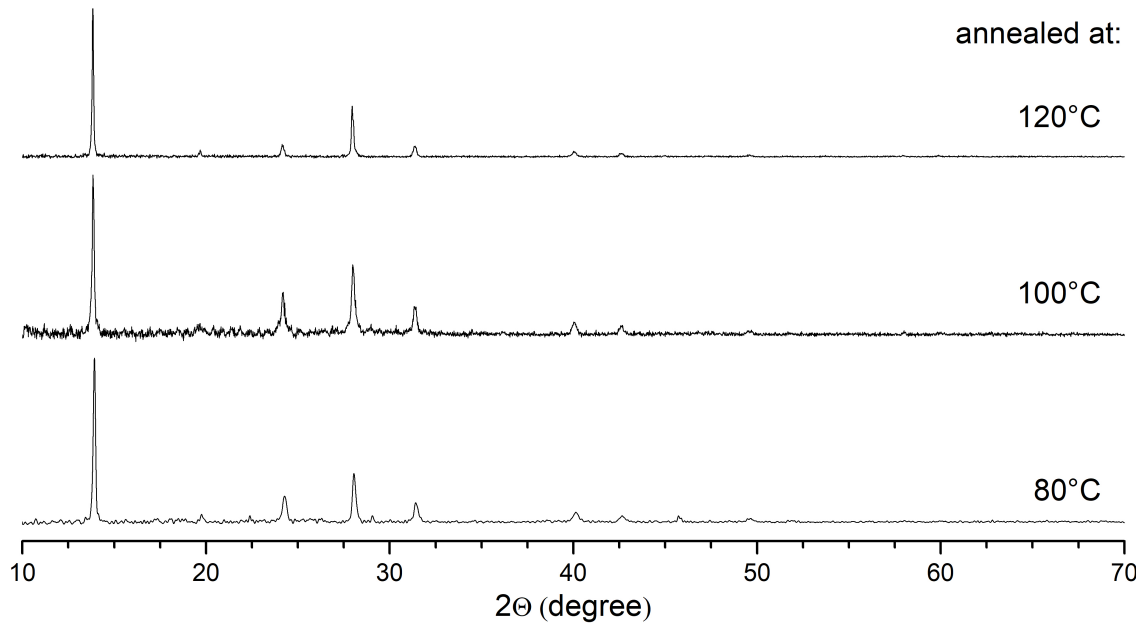


Figure 4.35: Experimental XRD patterns of as deposited $FAPbI_3$ thin films. The samples were annealed at different temperatures (80, 100, 120°C) after deposition.

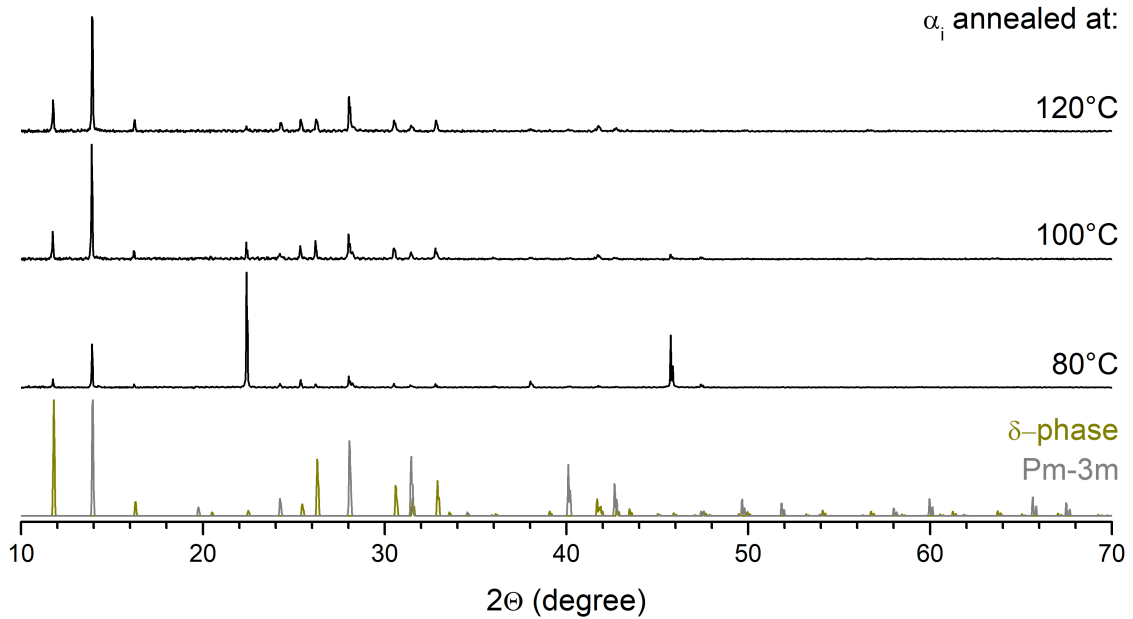


Figure 4.36: Experimental XRD patterns of degraded $FAPbI_3$ thin films. The samples were annealed at different temperatures (80, 100, 120°C) after deposition. Le Bail simulated patterns of the cubic phase (grey) and δ -phase (yellow) are included below.

Nomenclature: For simplicity, the sample annealed after deposition at a temperature $X^\circ\text{C}$ ($X = 80, 100, 120$) will be referred to as S_X , and that subindex added to any property keeps its relation with the annealing temperature.

The process from the precursor solutions to the α_{rec} polymorph in thin films is schematized in Fig. 4.38. The measurements were undertaken at RT immediately after each sub-process and the transitions are proposed based on the composition presented in Table 4.12.

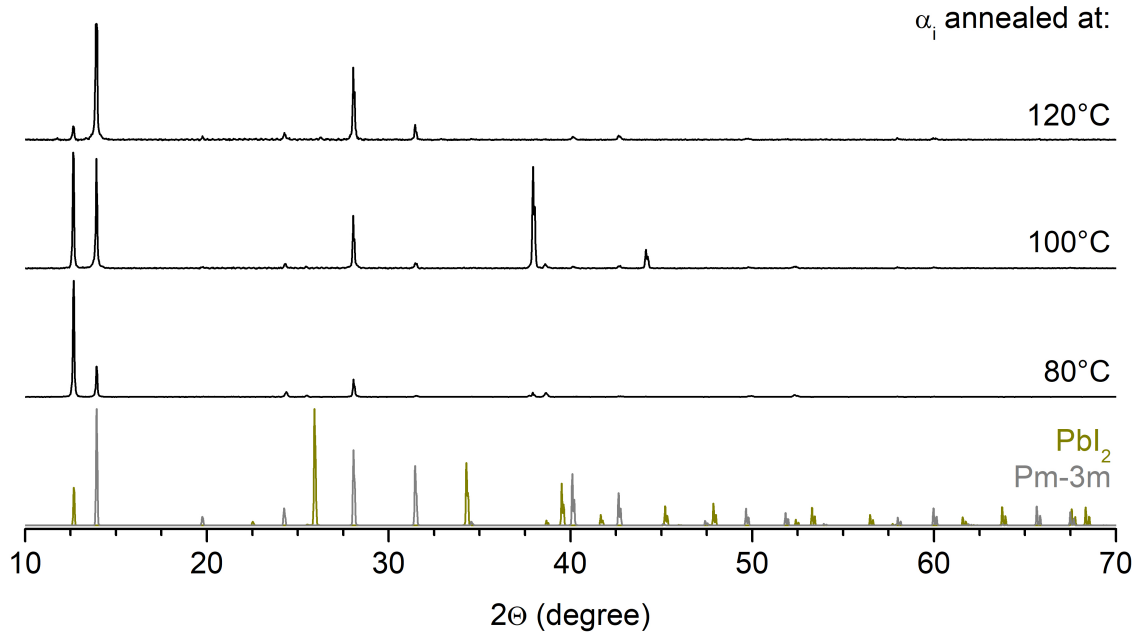


Figure 4.37: Experimental XRD patterns of thermally recovered $FAPbI_3$ thin films. The samples were annealed at different temperatures (80, 100, 120°C) after deposition. Le Bail simulated patterns of the cubic phase (grey) and PbI_2 (yellow) are included below.

Table 4.12: XRD analysis of $FAPbI_3$ thin films fitted with the LeBail method: lattice parameter (Å) and composition (%) of each phase .

State	Phase	Å (%)	Annealing temperature of α_i			Mean Value (Å)
			80°C	100°C	120°C	
as-deposited	α_i ($Pm\bar{3}m$)	a	6.357 (100.00)	6.376 (100.00)	6.384 (100.00)	6.372 (100.00)
degraded	α_δ ($Pm\bar{3}m$)	a	6.362 (18.96)	6.366 (23.80)	6.357 (2.20)	6.361 (20.99)
	δ ($P6_3mc$)	a	8.685	8.685	8.677	8.682
		c	7.929 (81.04)	7.929 (76.20)	7.928 (79.80)	7.929 (79.01)
		c				
thermally recovered	α_{rec} ($Pm\bar{3}m$)	a	6.349 (76.77)	6.355 (77.93)	6.355 (97.72)	6.353 (82.47)
	PbI_2 ($P\bar{3}m1$)	a	4.945	4.739	4.743	4.809
		c	6.979 (23.23)	6.986 (22.07)	6.983 (7.28)	6.983 (17.53)
		c				

Comparatively, all samples present a similar percentage of δ -phase (ca.80%) but different PbI_2 content. S_{80} and S_{100} have around 20%, while S_{120} presents only 7%.

Analysis of the Pawley fitting of the XRD patterns is presented in Fig. 4.39 and was determined as follows. The Pb-I bond length in a cubic phase is calculated as half of the lattice parameter (see Fig. 4.39a). The Pb-I bond lengths from secondary phases were evaluated with the visualization software VESTA(see Fig. 4.39b) and follow the relation $\delta > PbI_2 > \alpha_\delta$ for 80°C and $\delta > \alpha_\delta > PbI_2$ for 100°C and 120°C. For the full width at half maximum (FWHM), the peaks selected due to their presence in all samples and the

involvement of the halide atoms in the plane, which are depicted at the right of Fig. 4.39c.

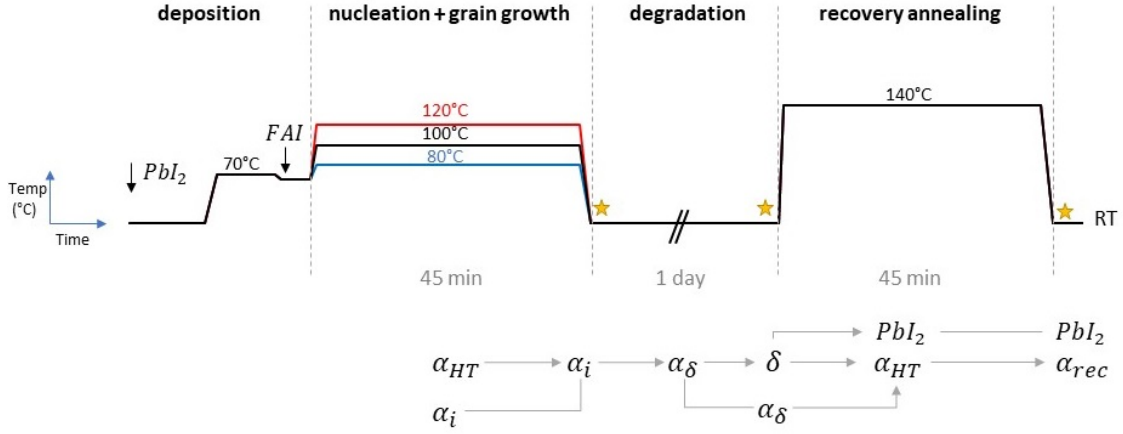


Figure 4.38: Scheme of evolution of $FAPbI_3$ from deposition until recovery annealing and their respective phase composition below. Star icons indicate the measurement points.

Deposition: The FAI solution is spin-coated over the PbI_2 film that has been deposited over the substrate and annealed at 70°C for 10 min.

Nucleation and grain growth: The new film is immediately annealed at the chosen temperature. The provided thermal energy is used for the perovskite nucleation and grain growth. The unit cell size of the cubic phase depends directly on the annealing temperature. Then, α_i presents the relation $a_{120} > a_{100} > a_{80}$. Also, if the annealing temperature is larger than the phase transition temperature (100-110°C), the perovskite will be structured as cubic $Pm\bar{3}m$ and nucleation will be favored instead of grain growth [See Chapter 3]. This results in fewer and larger grains in films annealed at lower temperatures. When the films are cooled to RT, the perovskite initially formed as α_{HT} converts into α_i and each one of the unit cells shrinks.

Degradation: During degradation the material phase aims towards δ due to its stability. This phase has a defined cell size at RT ($a = 8.682 \pm 0.001$ Å, $c = 7.928 \pm 0.005$, see Table 4.12), where the corresponding Pb-I bonds are 3.200 and 3.245 Å. The evolution of the lattice parameter from as-deposited to degraded can be explained by defining a converging Pb-I bond length. This value is calculated to be ca. 3.180: a_{80} (Pb-I=3.178Å) expands towards it while a_{100} (Pb-I= 3.188 Å) and a_{120} (Pb-I=3.192Å) shrink. Additionally, the magnitude of the variation of a is proportional to the relative difference $\Delta Pb - I = a_X/2 - 3.180[\text{Å}]$, which can be interpreted as internal stress. Theoretically, there is a temperature between 80°C and 100°C where the lattice size remains invariant through the transition.

The cubic cell size of SC can be roughly determined through the application of the relation $\omega = \sqrt{(k/m)}$ to the displacement of the Raman spectrum in each phase, as presented in Fig.4.39a. Qualitatively, the unit cell of α_i ($a=6.357$ Å) expands to transform into α_δ , where the Pb-I bonds are equal to the δ -phase. This likely occurs due to the shrinking of the cubic phase previous to the nucleation of the δ -phase, which starts close to the crystal

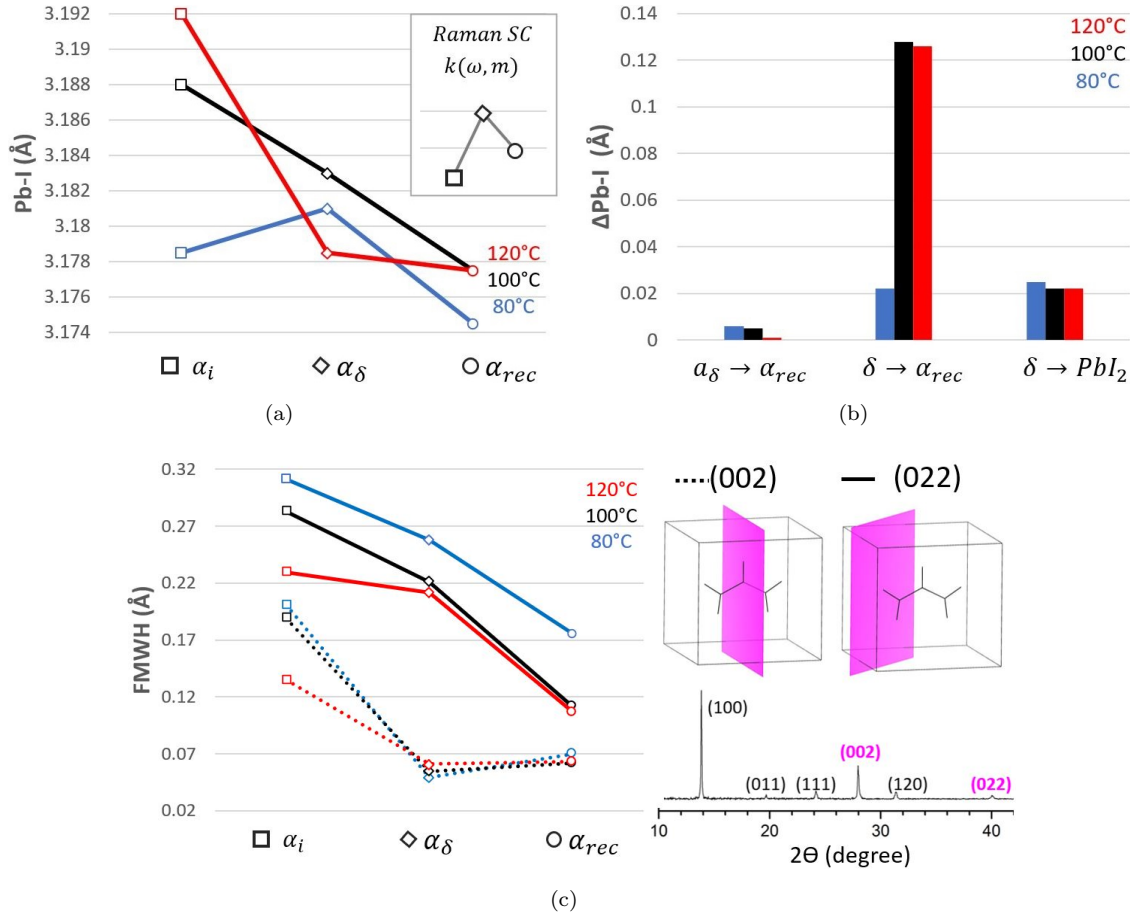


Figure 4.39: Analysis of the results obtained from Pawley refinement of the XRD patterns at RT: (a) Pb-I bond lengths of cubic ($Pm\bar{3}m$) phases, (b) shrinking of Pb-I bond during phase transitions from degraded to thermally recovered and (c) FWHM values for the corresponding (002) and (022) diffraction maxima. On the abscissa, three polymorphs of the samples are given: as-prepared (α_i), degraded (α_δ) and recovered (α_{rec}).

geometric center and expands towards the surface. In thin films, this situation does not occur because of the planar disposition of the α_δ -phase that allows the δ -phase to nucleate faster since it is already at the surface level.

Recovery annealing: In SCs, the cubic phase shrinks after the recovery annealing, which is also the case with thin films. When the sample is heated, three transformations take place: $\alpha_\delta \rightarrow \alpha_{HT} \rightarrow \alpha_{rec}$, $\delta \rightarrow \alpha_{HT} \rightarrow \alpha_{rec}$ and $\delta \rightarrow \text{PbI}_2$. The differences in Pb-I bond length for each transition are presented in Fig. 4.39b. This analysis indicates that the largest variations in bond length occur during the $\delta \rightarrow \alpha_{HT} \rightarrow \alpha_{rec}$ at 100°C and 120°C, resulting in equal Pb-I bond lengths. The PbI_2 generated from the reorganization of the perovskite is slightly smaller than pure PbI_2 , $3.073 \pm 0.001 \text{ \AA}$ vs $3.095 \text{ \AA}$ [94], which likely means that it is under compressive stress. By the contrary, the sample annealed at 80°C presents a PbI_2 far larger ($3.178 \text{ \AA}$) but closer to α_{rec} ($3.175 \text{ \AA}$).

For FWHM analysis, the selected peak planes are presented in Fig. 4.39c. The main plane (002) contains I and C while the plane (022) contains only I. Also, from the results of Raman spectroscopy, it is more probable that the halide atoms move along the plane (002)

while in (022) I^- ions cross the plane. With respect to the C atom, the rotation around the N-N axis and translation of the molecule maintains C in the plane. Hence, a higher intensity of plane (002) with respect to (022) is expected. The FWHM of the samples for both planes decreases from α_i to α_{rec} as a result of lower distortion or relaxation of tensile stresses. Comparing the annealing temperatures, $FWHM_{80} > FWHM_{100} > FWHM_{120}$ for α_i . Analyzing α_{rec} , $FWHM_{100}$ is similar to $FWHM_{120}$ which is likely the consequence of the same lattice size for both of them and indicates similar defectiveness. Since the PbI_2 content is larger (22%) for S_{100} than S_{120} (7%), the additional defectiveness of S_{120} likely comes from point defects. Therefore, lower performance is expected when applied to optoelectronic devices.

4.5.2 Performance dependence of optoelectronic devices

As concluded from the XRD measurement presented in Chapter 4.5.1, there is no significant difference in the lattice parameter of the cubic cell of $FAPbI_3$ regarding the annealing temperature ($\pm 0.005 \text{ \AA}$). This reflects in a neglectable variation of E_g that depends on the $Pb-I$ bond. The main effect of temperature is the defect density and the composition of the PbI_2 -phase, as deduced from the FWHM values.

In this Chapter, a sensitivity analysis is performed on a 1D simulation of a p-i-n solar cell using the software SCAPS (Solar Cell Capacitance Simulator)[15]. The model is based on the work of Karthick et al [53], where the conventional planar device architecture TCO/ETL/perovskite/HTL/Au is modeled. In this structure, the transparent conductive oxide is selected as FTO, Electron Transport Layer (ETL) as SnO_2 , and Hole Transport Layer as spiroOMeTAD due to the high device performance reported in the literature, especially for $FAPbI_3$ -based materials [77, 137] (See Fig. 4.40). Here, they varied parasitic series and shunt resistances to reproduce experimental data (thin films annealed at 150°C), where the performance of the device is greatly reduced compared to the simulated one. These resistances model the defect states (surface and interface) or some local inhomogeneity that produces charge recombination or current leakages.

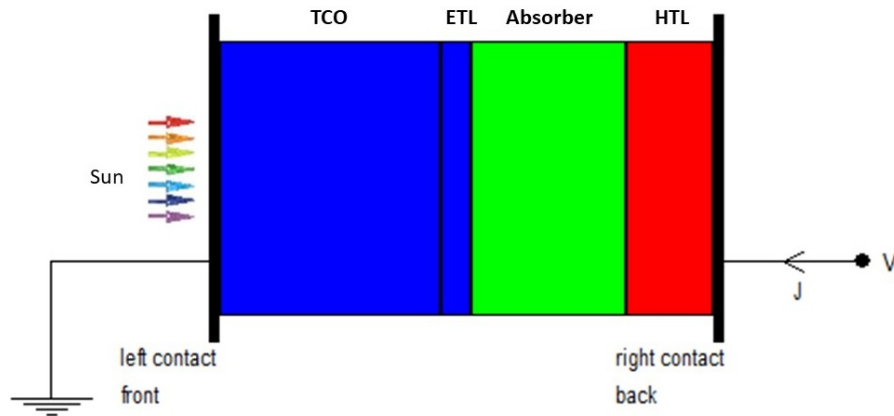


Figure 4.40: Model of p-i-n perovskite solar cell in SCAPS.

The input parameters are presented in Table 4.13, where the values of FTO, SnO_2 , FAPbI_3 (α) and Spiro-OMeTAD are taken from the referenced work [53]. Parameters of additional materials to simulate, PbI_2 and $\text{FAPbI}_3(\delta)$ are taken from single crystal data from references [93] and [45], respectively. Values that were not found for these compounds were reproduced from FAPbI_3 . It is worth noticing that the simulated FAPbI_3 is considered only as α , without distinction of its due to the varied source of parameters, e.g. recovered single crystals [37], and thin films annealed at 100°C [22] and 170°C [71].

Table 4.13: Input parameters used for the simulation of FAPbI_3 based perovskite solar cells [45, 53, 93]. D.O.S. refers to effective density of states.

Parameters	FTO	SnO_2	FAPbI_3 (α)	FAPbI_3 (δ)	PbI_2	Spiro- OMeTAD
Thickness (nm)	500	70	350	350	350	200
Band gap (eV)	3.5	3.5	1.51	2.88	2.41	2.9
e- affinity (eV)	4.0	4.0	4.0	4.0	3.2	2.2
Permittivity	9.0	9.0	6.6	6.6	10.4	3.0
D.O.S. at CB (cm^{-3})	2.2e18	2.2e17	1.2e19	1e19	1e19	2.2e18
D.O.S. at VB (cm^{-3})	2.2e18	2.2e17	2.9e18	1e19	1e19	2.2e18
e- thermal velocity (cm/s)	1e7	1e7	1e7	1e7	1e7	1e7
h+ thermal velocity (cm/s)	1e7	1e7	1e7	1e7	1e7	1e7
Mobility of e- (cm^2/Vs)	20	20	2.7	0.179	69.5	1e-4
Mobility of h+ (cm^2/Vs)	10	10	1.8	0.179	1.9	1e-4
n-type doping (cm^{-3})	1e15	1e15	1.3e16	3.1e11	1e15	0
p-type doping (cm^{-3})	0	0	1.3e16	3.1e11	1e15	1.3e18
Density of defects (cm^{-3})	1e18	1e18	4e13	4e13	4e13	1e15

The simulation is based on the classical drift-diffusion model and the operating conditions are 300K and one sun (AM1.5G, 100 mW cm^{-2}) irradiation. The optical absorption comes from the absorption coefficient model $\alpha(\lambda) = (1e5 + 1e12/h\nu)(h\nu - E_g)^{0.5}$ [15]. The adjacent interfaces to the absorber material are given the standard density of defects ($1e11 \text{ cm}^{-2}$). Applying the referenced parameters as input data, the same V_{OC} (1.2 eV) and PCE (21.4%) are obtained. A small difference in J_{SC} (22.6 vs 22.8 mA/cm^{-2}) and FF (77 vs 80.3%) may be a result of reduced significant digits or lack of specification in the defect properties.

A sensitivity analysis of solar cell performance with respect to the bandgap and density of defects is shown in Fig. 4.41. The range of bandgap goes from 1.48 to 1.62 eV, which is selected to cover the band gap values from $\alpha_i\text{-SC}$ to α_δ . The defect density is selected from literature, going as low as $1e11$ for SC [7, 45] to $1e16$ for MAPbI_3 [102]. Normally, $\alpha - \text{FAPbI}_3$ and mixed compounds are modeled with a density defect of magnitude around $1e13$ [52, 53, 116].

The main parameters do not present a high difference in values between defect density $1e11$ and $1e13$.

Open circuit voltage, V_{OC} , represents the maximum voltage that can be generated by the cell and depends on the number of charge carriers that reach each contact. The bandgap will vary the velocity to obtain V_{OC} but defects will tamper with the charge carrier transport. In this specific cell structure, a bulk defect density at the order of $4e15$ will damper V_{OC} to 1.0 from 1.17 V obtained at the nominal conditions ($E_g = 1.51\text{eV}$, defect density = $4e13\text{cm}^{-3}$).

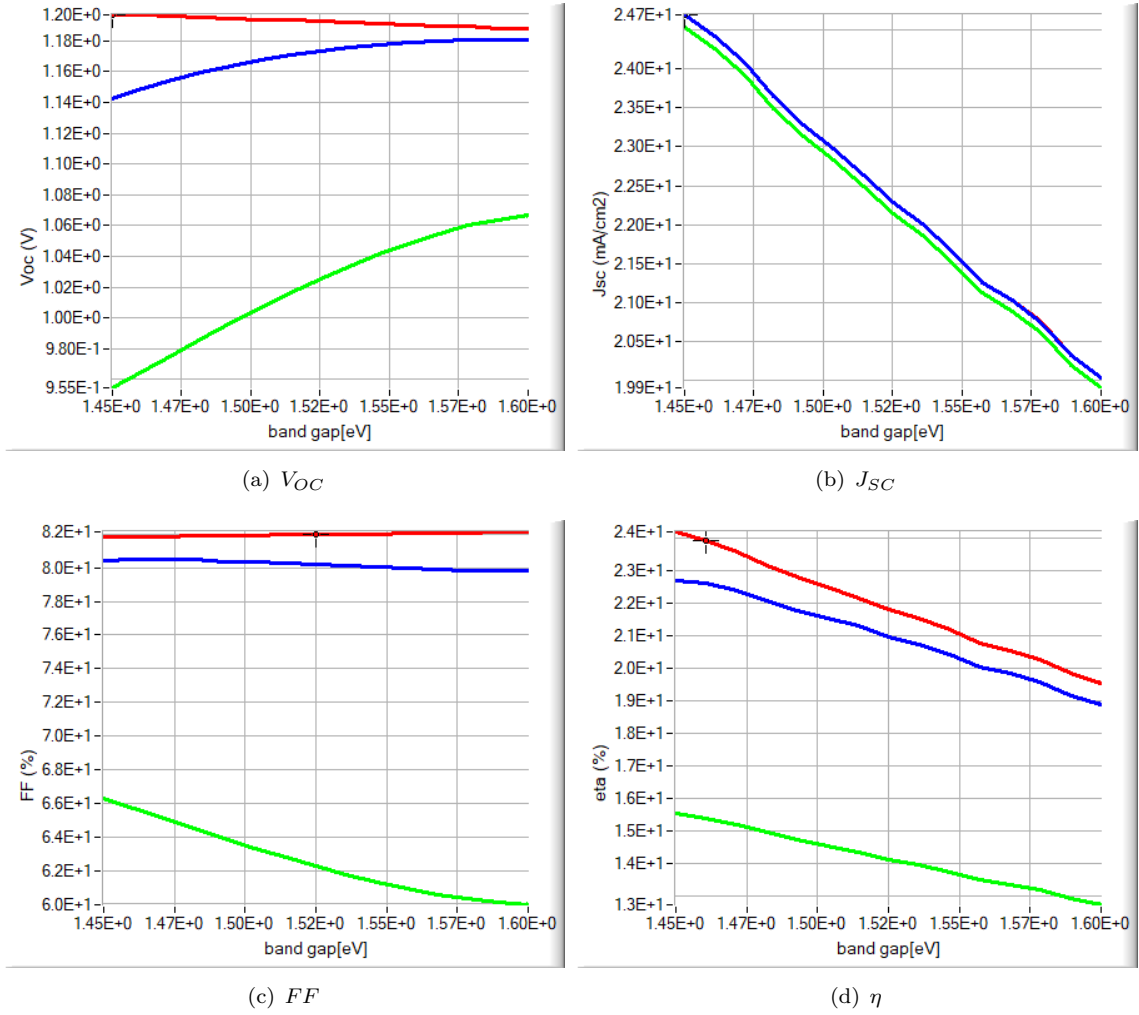


Figure 4.41: Main parameters dependence of band gap and density of bulk defects as given by the software. Line blue is the base line of defect density $4e13$, while red and green correspond to $4e11$ and $4e15$.

Short circuit current per area J_{SC} is practically invariant towards the defect density. It represents the maximum current that can be generated by the cell, i.e., it can be understood as the maximum quantity of charge carriers passing through an ideal connection. Then, it is expected that it depends directly on the bandgap, which regulated the number of carriers obtained per energy of the incident light.

Fill factor, FF , is the ratio between the maximum power point (MPP) current and voltage and $J_{SC}V_{OC}$. Then, it presents both dependencies. The highest level analyzed shows a stronger dependency on the defect density and bandgap, reducing FF from the nominal conditions 80% to 62%.

Power conversion efficiency (PCE) is the ratio of maximum generated power and the incident power. The curves show a similar tendency with respect to E_g . PCE at the nominal point is drastically reduced from 21.5 % to 14.5 %.

In conclusion, even though the efficiency may increase by 0.1 eV when reducing the defect density to a value close to the one of SC, the efforts should be redirected towards bandgap engineering. For example, epitaxial growth should be focused to stabilize the material rather than defect passivation or reduction. The sensitivity toward the bandgap is imperative. The transition of $\alpha_i \rightarrow \alpha_\delta$ increases significantly the bandgap (+0.1eV) which impacts the efficiency ca. 4%. Hence, a good stability strategy will prevent the variation of E_g .

As previously commented, the simulation in the reference work varied the parasitic resistance to model the experimental results of the $FAPbI_3$ solar cell [53]. A different model is proposed considering phase transitions and polymorphism α_δ , δ and PbI_2 . Two approaches are calculated: i) complete material transition along with the current flow and ii) nucleation of secondary phase at the interlayer, as presented in Fig. 4.42.

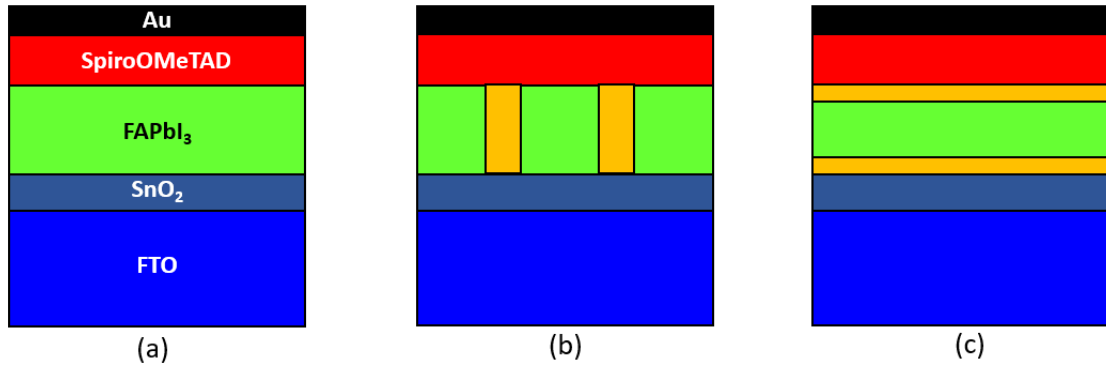


Figure 4.42: Simplified models of solar cell considering secondary phases (in yellow) and cubic phases (in green). a) reference model, b) material transition along the current flow, and c) nucleation of secondary phase at the interlayer.

4.5.2.1 Complete material transition along with the current flow

Since the model is 1D, it can be supposed that in local points, the degraded and recovered $FAPbI_3$ will present only the secondary phase. This means two additional models, Glass/FTO/ETL/ δ – $FAPbI_3$ /HTL/Au and Glass/FTO/ETL/ PbI_2 /HTL/Au. The model of the cubic phases of $FAPbI_3$ α_δ and α_{rec} are modeled equally to the α presented in literature since there is no distinction between them. The only variation will be made regarding the E_g of α_δ , where the value of the SC will be attributed (1.62 eV).

The main photovoltaic parameters of the experimental reference data and simulation of $FAPbI_3$ δ and α_δ , and PbI_2 are presented in Table 4.14.

From the calculated parameters, it is logical that no combination of phases will replicate the experimental values. For instance, FF and V_{OC} experimental data is lower than all the calculated ones. An interesting result is that a simple ponderated average of the degraded phases, 80% δ and 20% α_δ , results in a PCE of 4.2%, which is close to the experimental data.

The transformation along the absorber thickness would reflect, for example, secondary phases nucleating from grain boundaries. It is possible that the 1D model is insufficient to

Table 4.14: Main parameters of solar cell performance resulting from data input in Table 4.13. Experimental reference data is extracted from [53].

Parameters	Reference Exp	$FAPbI_3$ (α)	$FAPbI_3$ (α_δ)	$FAPbI_3$ (δ)	PbI_2
V_{OC} (V)	0.6	1.2	1.2	1.0	1.6
J_{SC} (mA/cm^{-2})	16.6	22.8	19.5	1.3	4.8
FF (%)	40.6	80.3	79.8	78.7	80.4
η (%)	4.3	21.4	18.3	1.1	6.3

capture the defectiveness of the interlayer between the two adjacent phases transversal to the current flow.

4.5.2.2 Nucleation of secondary phase at the interlayer

Another model to consider is the nucleation of a secondary phase between the absorber and the adjacent layers, where a higher defect density is expected. The simulation could only be performed for PbI_2 formed in the interlayer with HTL. Interfaces PbI_2/HTL , $FAPbI_3/PbI_2$ and $ETL/FAPbI_3$ were given a high defect density value of $1e16$ to inspect the impact on the model.

Table 4.15: Main parameters of solar cell performance resulting from data input in Table 4.13. Experimental reference data is extracted from [53]. Percentage indicates the proportion of PbI_2 thickness. The first result (*) is evaluated without interlayer defects.

Parameters	Exp	20%*	8 %	20 %	50 %
V_{OC} (V)	0.6	1.2	1.1	1.0	0.9
J_{SC} (mA/cm^{-2})	16.6	21.2	22.1	21.1	17.32
FF (%)	40.6	68.7	54.3	53.9	51.1
η (%)	4.3	17.8	12.9	11.9	8.6

First, the configurations that could not be simulated are analyzed. Fig. 4.43 shows the flat band diagram of the proposed solar cell. The energy of the Conduction Band (CB) and Valence Band (VB) of $FAPbI_3$ differ in literature. CB, VB pairs from experimental work are (-4.74,-6.24) and (-4.22,-5.63) obtained by photoelectron spectroscopy [144] and calculated from ionization energy and electron affinity measurements [117], respectively. In other hand, simulations gave (-4.0,-5.4) [53]. Due to the idealization of the simulation models and the variability of the experimental data with respect to the material deposition or synthesis, the middle value is selected (-4.22,-5.63). There is no information in the literature about CB and VB of the α_δ -phase, therefore, it is proposed a bilateral extension of the α bands fit the larger bandgap. CB and VB of PbI_2 are extracted from the work of Bae et al [5].

The injection of electrons from the perovskite layer towards the ETL and front contact relies on the alignment of the conduction bands. The CB of SnO_2 is close $FAPbI_3$, the difference of 0.2 eV attributed to the energy uncertainty. This close CB match is in order with the high-performance results of the nominal simulations. Both PbI_2 and δ -phase present CB energies to high compared to HTL, building an energy barrier for the carrier injection as

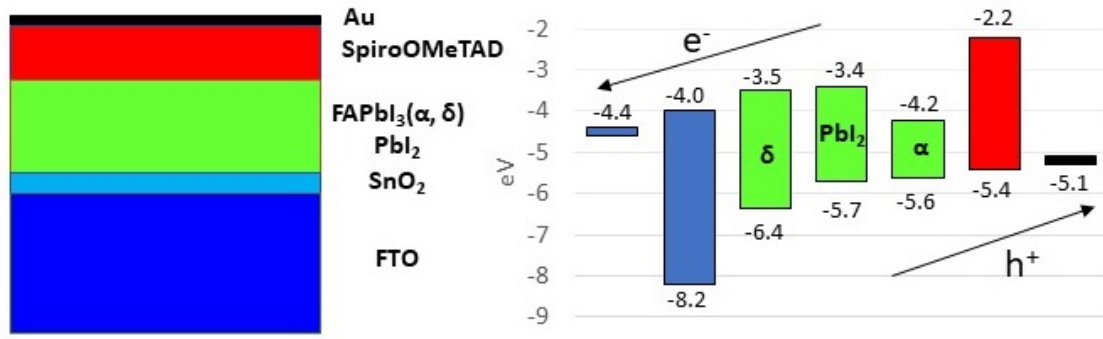


Figure 4.43: Simplified flat band energy diagram, with arrows indicating the charge transfer direction.

occurs in $MAPbI_3/PbI_2$ interfaces [5]. The interface $FAPbI_3$ /SpiroOMeTAD presents a good alignment, also differing in 0.2 eV. The presence of a PbI_2 layer in between would allow the carrier injection due to its similar VB to $FAPbI_3$. The VB of the δ -phase is estimated to be too low to allow the hole injection to the HTL.

Results from Table 4.15 show a decrease in the cell performance. The additional layer of PbI_2 reduces the light absorption, which will be reflected in the reduction of J_{SC} . Moreover, a high charge accumulation may occur inside the absorber layer, which explains the decrease in V_{OC} .

Considering that this approach reduces considerable the J_{SC} , a model combining both designs will be simulated. A PbI_2 layer of 20% of the absorbance thickness will be simulated for both δ and α_δ phases. The ponderated average (δ, α_δ) is considered for the base case, 80% of PbI_2 content, to match J_{SC} and to match η .

Table 4.16: Main parameters of solar cell performance for degraded phases with an interlayer of 20% PbI_2 adjacent to HTL. At right, percentage ratio δ/α_δ .

Parameters	Exp	δ	α_δ	80/20	7/93	65/35
V_{OC} (V)	0.6	1.0	1.1	1.1	1.1	1.1
J_{SC} (mA/cm^{-2})	16.6	2.0	17.6	5.1	16.6	7.4
FF (%)	40.6	50.7	53.1	51.2	53.0	51.6
η (%)	4.3	1.1	10.4	2.9	9.7	4.3

Results from Table 4.16 show a closer agreement with experimental data. Differences are attributed to uncertainty in input data and 2D effects out of the scope of the simulation software.

In conclusion, $FAPbI_3$ polymorphism is relevant to model optoelectronic devices and explains highly defective areas assumed by other models, such as the implementation of parasitic resistances.

4.5.3 Summary

In this Chapter, the understanding of $FAPbI_3$ polymorphism was applied to thin films.

The annealing temperature for the nucleation of $FAPbI_3$ from the precursor's solutions and grain growth was studied around the phase transition temperature. Below that temperature, the degradation and recovery do not generate high internal stress compared to after. The variation in the Pb-I bond length during the transition $\delta \rightarrow \alpha_{rec}$ is at least 6 times larger for annealing temperatures of 100°C and above. Even though the annealing at 80°C results in more PbI_2 content with respect to the 120°C, smaller cell size is recommended.

Solar cell performance is more sensitive to variations of bandgap than to the density of bulk defects. Two models were simulated for the nucleation of secondary phases: along and transversal of the current flow. The δ -phase is only expected to nucleate from α grains, probably in grain boundaries since the other configuration is not possible due to band misalignment. The simulated performance closer to the experimental data was the result of a PbI_2 in the interface between the perovskite and HTL.

The strong dependency of the polymorphism structure on the annealing temperature allows further optimization of the deposition process of thin films that would reflect better device performance.

Chapter 5

Conclusions and outlook

In this thesis, we investigated the vibrational spectrum of $FAPbI_3$ single crystals (SCs) and the optoelectrical properties of thin films. The analysis of Raman modes lead to conclusions about the material morphology and the structural stability, while the characterization of the films gave additional information about the defectiveness and size of the unit cell, allowing simulation models closer to experimental data.

In terms of morphology, we determined the cell structure and phase transitions and studied the interaction between the organic cation and the inorganic framework. For structural stability, we proposed mechanisms for the $\alpha \rightarrow \delta$ phase transition and the stability enhancement when elements are partially substituted. To determine the morphology and stability, SCs were characterized due to their considerably lesser compositional defects as compared to the films. Hence, we could discard from the analysis the presence of solvents and heterogeneous growth proper of thin films. The main characterization tool used was micro Raman spectroscopy. This was due to its non-destructive nature, which is fundamental considering the unusually high softness of LHPs compared to conventional semiconductors. The information obtained about chemical structure, phase transition, polymorphism, crystallinity, and bonds strength made this technique optimal for the understanding of hybrid compounds such as the perovskites. The analysis was supported experimentally by PL and XRD and theoretically by DFT calculations.

There is a myriad of applications of perovskite in optoelectronic devices, both as SC and thin film. One of the most notorious is the solar cell due to its accelerated performance improvement since its first publication. However, there is no established method to deposit perovskites in the literature, varying the precursor solutions, deposition method, and operating conditions of deposition, among others. One of the most used deposition methods is spin-coating, after which the annealing of the perovskite takes place. Then, we analyzed the effect of the annealing temperature on the lattice parameter and phase content in each polymorph, which is related to the key parameters bandgap and defectiveness. The chosen technique was XRD due to the ability to distinguish phases structures and composition. Using simulation software, the sensitivity toward band gap and defect density of different architectures of the solar cell were determined.

5.1 Vibrational spectra

We disclosed experimentally the Raman spectrum of $FAPbI_3$ (all polymorphs at RT and the phase at 200°C), $FAPbBr_3$, $Cs_{0.1}FA_{0.9}PbI_3$ and $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$. We calculated through DFT the Raman modes of MA^+ , FA^+ , $FAPbI_3$ and $FAPbBr_3$.

The high frequency region of Raman spectra of $MAPbI_3$ and $MAPbBr_3$ ($> 800\text{ cm}^{-1}$) can be totally attributed to the Raman modes of the isolated MA^+ . Analogous is the case of $FAPbI_3$ (α_δ and δ) and $FAPbBr_3$ ($> 500\text{ cm}^{-1}$) towards the isolated FA^+ .

In terms of Raman modes, we divided the Raman spectrum in three parts: octahedral modes ($< 50\text{ cm}^{-1}$ for I-based and $< 65\text{ cm}^{-1}$ for Br-based), molecular modes ($> 500\text{ cm}^{-1}$) and perovskites modes in between. The low-frequency modes are O_h symmetry modes, twist, and distortion, while the high-frequency zone equals the isolated molecules modes but presents shifts. The medium frequency zone result from molecular reorganization and the consequent octahedral response. They are in-plane and out-of-plane rotations and symmetric and asymmetric out-of-plane bending.

5.2 Morphology

The cell structure of the $\alpha - FAPbI_3$ is cubic $Im\bar{3}$. Herewith, the molecules organize head-to-tail, generating an eight-fold of cubic unit. The phase transition to the cubic $Pm\bar{3}m$ symmetry occurs around 100-110°C (α_{HT}). From there, the molecules rotate spherically without distortion due to the thermal expansion of the lattice.

In literature, the material is synthesized, degrades along the day, and then is recovered by annealing. This results in the polymorphism of the widely known α phase at room temperature: as-synthesized or initial (α_i), degraded (α_δ), and thermally recovered (α_{rec}). They are all photoactive and exhibit the transition to α_{HT} , but differ in the level of distortion. This affects the stability and lattice constant, which both varies in the trend $\alpha_\delta > \alpha_{rec} > \alpha_i$. Other consequences are the band-gap and the intensity of the PL signal, which are relevant for device performance. Specifically, the degraded material presents simultaneously two phases, α_δ and δ , while the thermally recovered presents α_{rec} and PbI_2 .

Regarding the interaction between the organic cation and the surrounding octahedra, we proved the absence of hydrogen bonding in lead halide perovskites. In consequence, several properties that were previously attributed to hydrogen bonding have to be again understood. Among them, we find surface passivation, structural stability of mixed cation compounds, structural instability of $FAPbI_3$, and ferroelectric behavior. We found hydrogen bonds in FAI salt powder at temperatures below -100°C, which we suggest is the common N-H...N bonds for amines. Temperature-dependent measurements of $FAPbBr_3$ and $MAPbBr_3$ showed the absence of this directional bonding at any temperature lower than 25°C. We also proved that the criterion employed can be used for hybrid compounds.

5.3 Stability

The mechanism and trigger of the instability $\alpha \rightarrow \delta$ are explained in the following.

How? Initially, the cell of $FAPbI_3$ expands and generates defects. There, the octahedra are driven to merge, encircling two organic cations per unit cell. This is the nucleation of the δ -phase. Since the octahedra in the δ -phase are smaller than the ones in the α_δ -phase, this secondary phase becomes a stress release zone for the α_δ -phase and expands.

Why? As presented before, we already discarded hydrogen bonding as the reason for the phase transition. Then, it is more likely associated with structural factors such as stress. We suggest that vibration "molecular rotation around N-N axis" is the main factor. The planar disposition of the FA^+ molecules plays an important role in the $FAPbI_3$ packing. Then, this volumetric rotation distorts the already constricted structure, keeping the charge movement low and delaying the I^- ions response. Then, the cell expansion is triggered to accommodate the rotating molecules.

The enhanced stability of the thermally recovered polycrystal and the mixed compounds can be explained in the same fashion. In both, the main factor is the contribution of local defects to fit the larger $FAPbI_3$ structure. In the recovered sample, the PbI_2 and grain boundaries act as the stress release zones. In the mixed compounds, $Cs_{0.1}FA_{0.9}PbI_3$ and $Cs_{0.1}FA_{0.9}PbI_{2.6}Br_{0.4}$, this role is fulfilled by the distribution of Cs^+ and Br^- in the $FAPbI_3$ matrix. Additionally, the Cs^+ and FA^+ cations are coordinated, favoring the atomic displacement and decreasing the FA^+ rotation.

5.4 Thin film characterization

The planar disposition of thin films and small grain size allows a separation of the second phase formation and cubic phase size variation, which is constricted in SCs. The annealing temperature below the transition temperature (100-110°C) results in lower lattice size and larger defects. Samples annealing above that temperature results in similar lattice size and defectiveness varying in phase composition. The lower percentage of PbI_2 indicates a larger density of point defects.

The modeling of optoelectronic devices should contemplate the polymorphism of PbI_2 to obtain results closer to experimental without adding defects of uncertain precedence. The best performance is obtained for annealing below the transition temperature due to its lower cell size and consequentially, bandgap. This is based on a larger dependence of solar cell parameters on bandgap variations than on the density of bulk defects. Simulations closer to experimental results would allow optimizations of the deposition process.

5.5 Outlook

The understanding of vibrational dynamics in hybrid perovskites could bring additional assets in the development of new and stable structures. Some ideas are presented in the following.

- The identification of the suitable lattice constant for a stable structure would help with the substrate selection for epitaxial growth of $FAPbI_3$ thin films.
- The engineering of new structures can also be helped by knowing the stability conditions, critical temperatures, and the lack of hydrogen bonding in lead halide perovskites.
- Further optimization of stability strategies can be made through the study of the Raman spectra of new compositions, determining the stability before the application in the device.
- The understanding of the dynamics of non-spherical geometry of organic A-cations may also be useful for substituting formamidium, either partially or totally.
- The grain size, annealing time, and optoelectronic properties can be measured in thin films for the same conditions exposed previously to support or rectify the conclusions obtained from XRD.
- The annealing temperature of thin films can be extensively studied for both steps of spin-coating deposition to obtain an optimum value compromising lattice size and defectiveness.
- A solar cell can be created with $FAPbI_3$ thermally recovered to study its performance and stability.

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