

Development of a Compact Sample Environment for In Situ X-ray Scattering During Spin-Coating of Hybrid Materials and First Tests

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Abstract

Hybrid organic materials are widely investigated due to their exceptional optical properties, high structural flexibility and low-cost production. X-ray scattering techniques are non-invasive methods which allow studying crystallization kinetics *in situ* during thin film growth, unraveling the processes occurring between the deposited solution (liquid state) and final film (solid state). In order to achieve high spatial and temporal resolution, the X-rays at synchrotron facilities have to be used. This requires a special sample environment with various remotely controlled systems to be installed at the diffractometer.

This work is focused on the development of a compact sample environment for studying hybrid organic-inorganic materials by *in situ* grazing incidence X-ray scattering (GIWAXS) and revealing crystallization kinetics during spin-coating and subsequent annealing. The spinning motor features speeds from 500 rpm up to 10000 rpm with a low "wobbling" amplitude, which ensures the stability of the angle of incidence during the scattering experiments. The annealing for completing thin film crystallization is done by a halogen lamp targeted at the sample surface. For monitoring the optical properties of thin films, differential reflectance spectroscopy (DRS) was adjusted to the spin-coating chamber. The detailed description of each system designed and introduced into the chamber is provided. All systems used for sample deposition and characterization are remotely controlled via TANGO. The chamber was successfully integrated and tested at the Deutsches Elektronen-Synchrotron (DESY) and European Synchrotron Radiation Facility (ESRF).

For the demonstration of the designed chamber performance, the materials used as active layers for solar cells, namely organic-inorganic perovskites, were deposited as thin films using three solution-based methods: one-step deposition, antisolvent-assisted and gas quenching methods. The crystallization kinetics of various perovskite compositions from precursor solutions were studied by *in situ* GIWAXS depending on the cations and halides. The research of this work highlights the influence of different cations and halides on the pathways of the three-dimensional (3D) perovskite phase formation. Besides that, two-dimensional (2D) perovskite compositions with various spacer and small cations were studied, the interplay of the forming phases and their preferred orientations was analysed and summarized. In particular, annealing profiles directly affect the orientation of spacer cations in 2D perovskite phases.

The designed chamber is essentially only a beginning of the journey to reveal the crystallization complexity of thin films, deposited from solution. The acquired structural information during real-time experiments can be used for the optimization of the deposition procedures, tracking the influence of different conditions on the film quality, and avoiding the unnecessary and detrimental phases.

Deutsche Zusammenfassung

Hybride organische Materialien werden aufgrund ihrer außergewöhnlichen optischen Eigenschaften, ihrer hohen strukturellen Flexibilität und ihrer kostengünstigen Herstellung umfassend untersucht. Röntgenstreutechniken sind nicht-invasive Methoden, die es ermöglichen, die Kristallisationskinetik während des Dünnschichtwachstums *in situ* zu untersuchen und die Prozesse zwischen der abgeschiedenen Lösung (flüssiger Zustand) und dem endgültigen Film (fester Zustand) zu entschlüsseln. Um eine hohe räumliche und zeitliche Auflösung zu erreichen, müssen Röntgenstrahlen von Synchrotron Anlagen genutzt werden. Dies erfordert eine spezielle Probenumgebung mit verschiedenen ferngesteuerten Systemen, die am Diffraktometer installiert werden müssen.

Diese Arbeit konzentriert sich auf die Entwicklung einer kompakten Probenumgebung zur Untersuchung hybrider organisch-anorganischer Materialien durch Röntgenstreuung mit streifendem Einfall (GIWAXS) und zur Aufdeckung der Kristallisationskinetik während der Schleuderbeschichtung und des anschließenden Ausglühens. Der Motor verfügt über Drehzahlen von 500 rpm bis zu 10000 rpm mit einer geringen "Taumel"-Amplitude, was die Stabilität des Einfallswinkels während der Streuexperimente gewährleistet. Das Heizen zur Vervollständigung der Kristallisation der Dünnschicht erfolgt mit einer auf die Probenoberfläche gerichteten Halogenlampe. Zur Überwachung der optischen Eigenschaften der Dünnschichtfilme wurde die Differenzialreflexionsspektroskopie (DRS) an die Spin-Coating-Kammer angepasst. Jedes System, das entwickelt und in die Kammer eingeführt wurde, wird ausführlich beschrieben. Alle für die Probenherstellung und -charakterisierung verwendeten Systeme werden über TANGO ferngesteuert. Die Kammer wurde erfolgreich integriert und am Deutschen Elektronen-Synchrotron (DESY) und an der European Synchrotron Radiation Facility (ESRF) getestet.

Zur Demonstration der Leistungsfähigkeit der entworfenen Kammer wurden die als aktive Schichten für Solarzellen verwendeten Materialien, nämlich organisch-anorganische Perowskite, mit drei lösungsbasierten Methoden als dünne Filme hergestellt: Ein-Schritt-Herstellung, Antisolvent-unterstützte und Gas-Quenching-Methoden. Die Kristallisationskinetik ausgewählter Perowskit-Zusammensetzungen aus der Vorläuferlösung wurde mittels *in situ* GIWAXS in Abhängigkeit der Kationen und Halogeniden untersucht. Die Untersuchungen dieser Arbeit zeigen den Einfluss verschiedener Kationen und Halogenide auf die Wege der dreidimensionalen (3D) Perowskitphasenbildung. Darüber hinaus wurden zweidimensionale (2D) Perowskit-Zusammensetzungen mit verschiedenen Spacern und kleinen Kationen untersucht, das Zusammenspiel der sich bildenden Phasen und ihre

bevorzugten Orientierungen analysiert und zusammengefasst. Insbesondere wirken sich Heizprofile direkt auf die Orientierung von Spacer-Kationen in 2D-Perowskit-Phasen aus.

Die entworfene Kammer ist im Grunde nur ein Anfang auf dem Weg, die Komplexität der Kristallisation von dünnen Schichten, die aus einer Lösung hergestellt werden, aufzudecken. Die während der Echtzeit-Experimente gewonnenen Strukturinformationen können für die Optimierung der Herstellungsverfahren genutzt werden, um den Einfluss verschiedener Bedingungen auf die Filmqualität zu ermitteln und unnötige und schädliche Phasen zu vermeiden.

(Korrekturleser: Niels Scheffczyk)

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Part I.

Introduction and Theory

1. Introduction

1.1. Scientific background and motivation

X-ray scattering methods are widely used for an insightful structural characterization of different materials during and after the deposition procedure. The preliminary structural analysis of thin films can be conducted in a laboratory with a typical X-ray tube that emits $\text{Cu}_{K\alpha}$ line radiation (8.04 keV beam energy). The high brilliance of modern synchrotrons allows to observe thin film growth with high spatial and temporal resolution in real time by monitoring the scattering intensity evolution [1, 2]. In order to achieve surface sensitivity, grazing incidence X-ray scattering methods, i.e. scattering under small angle of incidence $\alpha_i = 0\text{--}1^\circ$, are used as a powerful tool for structural characterization which includes crystal structure, polymorphism [3], mosaicity [4], preferred domain orientation [5], crystallinity [6] and in-plane texture [7]. A focused beam with high spectral brightness is required to provide the improved temporal and lateral resolution needed to study crystallization processes during thin film deposition and solidification. High brilliance X-ray sources offer a wide variety of scattering methods to study structural properties in a non-invasive manner *in situ*, such as thin film crystallization kinetics, thickness and roughness evolution, phase transformation, scattering domain size and preferred domain orientation [8].

Typically, synchrotron facilities include numerous beamlines, each of them is dedicated to a specific kind of scattering experiment with the desired geometry (Fig. 1.1). Some beamlines offer X-ray beams with a specific photon energy, which can be focused (its size can be adjusted to specific needs), a diffractometer, which often includes a sample holder, or an option to fix a custom-built sample environment, and various X-ray photon detectors. Experimental setup, such as heating stage covered with a dome made of any X-ray transparent material, allows surface and structural characterization in an inert atmosphere or in vacuum. On the other hand, thin film growth experiments require designing a chamber with various embedded systems, which have to be remotely controlled. Numerous requirements and restrictions must be considered in the framework of instrumental engineering, introduced by a limited space on the diffractometer and various nuances of the grazing incidence geometry. In order to characterize the full growth procedure of different materials at synchrotron facilities, different sample environments were developed in the past. Those include chambers for deposition of the material in vacuum [9–12], as well as solution-based [13–16] thin film fabrication methods, or chemically inert chamber for

oxidation process analysis of thin films [17].

Solution-based procedures are broadly used for organic thin film fabrication, including spin-coating, spray-coating, dip-coating, blade-coating and roll-coating [18, 19]. These methods are established for depositing thin films with good homogeneity and low surface roughness. Spin-coating is one of the vital routes for laboratory-scale sample fabrication. The method is rapid and simple, yet it provides an optimal thin film morphology and thicknesses ranging from a few nanometers to a few micrometers [20]. A typical one-step spin-coating method is displayed in Fig. 1.2. A wide range of materials can be studied during spin-coating, for example, polymer thin films [21–23], small-molecule organic semiconductors [24, 25], coupled organic-inorganic nanostructures (COINs) [26, 27] and perovskite thin films [28–35].

Present thesis includes a complete description of all systems within the designed cham-

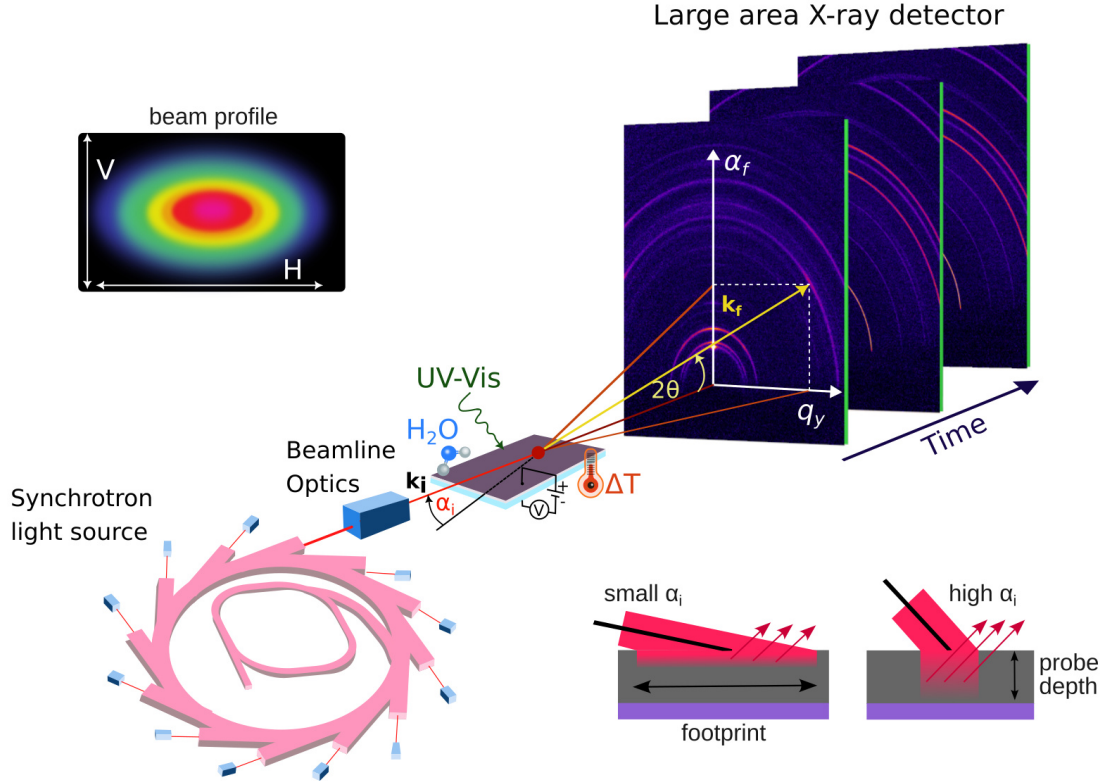


Figure 1.1.: Illustrative overview of the synchrotron-based grazing incidence X-ray scattering experiment for tracking crystallization *in situ* and *in operando*. Details on the X-ray scattering experiment: synchrotron beam profile, characterized by horizontal (H) and vertical (V) sizes (top left); dependence of beam footprint and penetration depth on the angle of incidence α_i (bottom right). By reaching the target structure, characterizing phase mixtures and controlling deposition parameters, one can achieve an optimal experimental procedure. Adapted from [8].

ber for *in situ* spin-coating experiments [36] and a demonstration of its performance for

various perovskite compositions, produced by different spin-coating methods [37–39]. The acquired knowledge aims at providing a better understanding of the processes that occur during thin film crystallization, depending on the precursor composition and deposition method, as well as the annealing and atmosphere parameters utilized.

Organic-based materials are often deposited from a precursor solution, so tracking

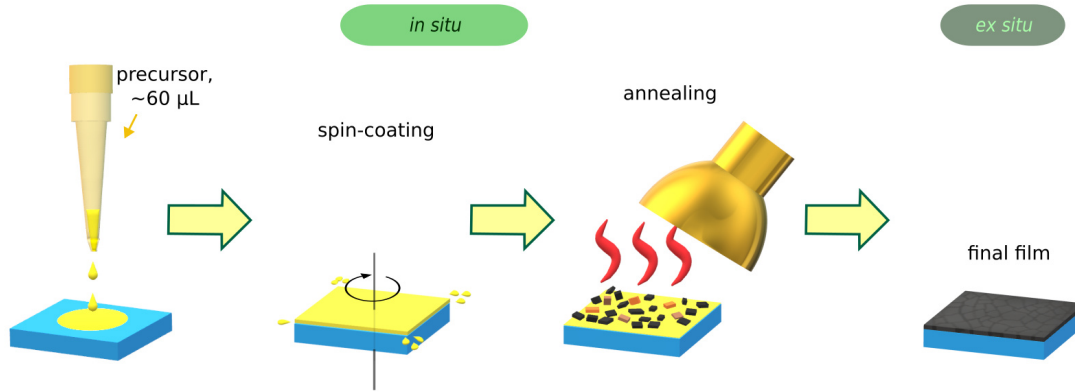


Figure 1.2.: Conventional spin-coating method with annealing used as post processing step with marked synchrotron-based X-ray scattering experiments for tracking crystallization *in situ* and studying the resulting film *ex situ*.

their crystallisation from the liquid state to the solid thin film is valuable for designing and fine-tuning the target structure to meet the requirements for use in the industry of optoelectronics. One of the most promising materials to be used as an active layer in solar cells are organic-inorganic perovskites [40]. The modification of their composition leads to the adjustment of the material band structure, which is one of the keys of achieving multifunctional and efficient optoelectronic devices [41]. A clear benefit of perovskite thin films in comparison to silicon-based solar cells is the possibility of the low-temperature fabrication from precursor solution. Spin-coating is a common technique for perovskite thin film fabrication, with active utilization in the laboratory-based preparation of photoactive layers [23]. Detection of the crystallization pathways using X-ray scattering methods provides essential information on the formation mechanisms, including solvent-based [42] and solid non-perovskite phases [43], which influence both thin film quality and perovskite phase stability. The *in situ* scattering experiments provide an essential knowledge about the thin film structure during deposition, while *ex situ* measurements with the variation of the angle of incidence enable the investigation of the surface layer of the thin film as well as the examination of its entire depth down to the substrate. The tracking of crystallization in thin films is also of significance for the study of the preferred orientation of the target phases, which are of essential importance for the optoelectronic properties [44].

1.2. Structure of this thesis

This thesis is divided into three parts: Part I: Introduction and Theory, Part II: Results and Discussion and Part III: Appendix.

Part I Chap. 2 provides scientific background on X-ray scattering, the features of grazing incidence geometry and methods used for *in situ* structural analysis of thin films. This chapter also includes experimental details on spin-coating as a common technique for solution-based thin film deposition. Chap. 3 gives a brief description of perovskite structure studied in the present work as an example of hybrid organic-inorganic materials.

Part II Chap. 4 describes in detail all systems of the designed spin-coating chamber for *in situ* X-ray scattering[36] and provides a full assembly instruction for the designed spin-coating chamber, including both hardware and electronics. The Chap. 5 starts with the crystallization kinetics of various 3D perovskite compositions including one to four cations and one to two halides, and is followed by an additional research on an observed solvent-based intermediate phase, conducted using the designed chamber, described in previous chapter. Besides that, Chap. 5 includes the first tests of the films deposited by three different methods: one-step conversion, antisolvent-assisted deposition and gas quenching treatment, with compositions featuring one to three cations and one to two halides. Chap. 6 displays the influence of different cations and halides as well as different spacer cations on growth kinetics of 2D perovskite compositions and preferred orientations of the formed 2D phases. Chap. 7 highlights the main results of the present work, and gives a brief overlook on the potential improvements and future measurements.

Part III Appendix A includes an additional information related to the designed chamber, which is described in Chap. 4. Appendix B contains additional figures, related to Chap. 5, which show the results of the X-ray scattering data analysis as well as raw data with marked structures, and are not critical to support the conclusions but might still be useful to the reader. Appendix C shows an additional analysis of the data presented in Chap. 6 and is not crucial for supporting the conclusions. Appendix D provides a complete table of all of the scattering data sets used in this work, including information about when and where the data was acquired. Also, a list of all acronyms used in this work can be found at the end of the Appendix.

The Appendix includes the bibliography as well as a list of all publications by the author of this thesis.

2. Experimental methods

2.1. X-ray scattering theory

2.1.1. X-ray basics*

The discovery of X-rays by the German physicist Wilhelm Conrad Röntgen [46] led to the development of new medical imaging techniques and a major advance in crystallography, making X-rays the most widely used type of radiation today, surpassing neutron and electron beams. X-rays are a type of electromagnetic radiation with a much shorter wavelength than visible light, about 1 Å (1×10^{-10} m). This makes them well suited for experiments on scattering from atomic lattices. A plane monochromatic X-ray wave is displayed in Fig. 2.1. It is assumed that the beam travels along the z -axis, perpendicular to the electric field, $\mathbf{E}$, and the magnetic field, $\mathbf{H}$. Due to the fact that magnetic field can be uniquely determined from the electric one, we will focus solely on the electric field and disregard the magnetic field, because $|\mathbf{E}| / |\mathbf{H}| = c \gg 1$. Given its classical nature, the spatial dependence of the electromagnetic field at a given instance of time can be described by the wavelength λ or, alternatively, by the wave number $k = 2\pi/\lambda$. One way to mathematically express the amplitude of the electric field is as a harmonic wave that periodically repeats every 2π with the spatial period λ , either in its real form, $E_0 \sin(kz)$, or in its compact complex form, $E_0 e^{ikz}$. The temporal and spatial variation of a plane wave travelling along the z -axis can be expressed in a single equation: $E_0 e^{i(kz - \omega t)}$. For the case in three dimensions, the polarization of the electric field is represented by a unit vector $\hat{\mathbf{e}}$ and the wave vector along the direction of propagation is denoted by $\mathbf{k}$, so that:

$$\mathbf{E}(\mathbf{r}, t) = \hat{\mathbf{e}} E_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \quad (2.1)$$

Due to the transverse nature of electromagnetic waves, we have $\hat{\mathbf{e}} \cdot \mathbf{k} = 0$, and $\mathbf{k} \cdot \mathbf{E} = \mathbf{k} \cdot \mathbf{H} = 0$, as displayed in Fig. 2.1.

The relation between wavelength λ in Å and photon energy $\mathcal{E}$ in keV valid for X-rays can be written as:

$$\lambda[\text{\AA}] = \frac{hc}{\mathcal{E}} = \frac{12.398}{\mathcal{E}[\text{keV}]} \quad (2.2)$$

An X-ray photon can interact with an atom by either being scattered or absorbed. In situations where X-rays interact with a dense medium consisting of a vast number of atoms

*Most of the contents of this paragraph are adapted from the book [45]. Other references are indicated.

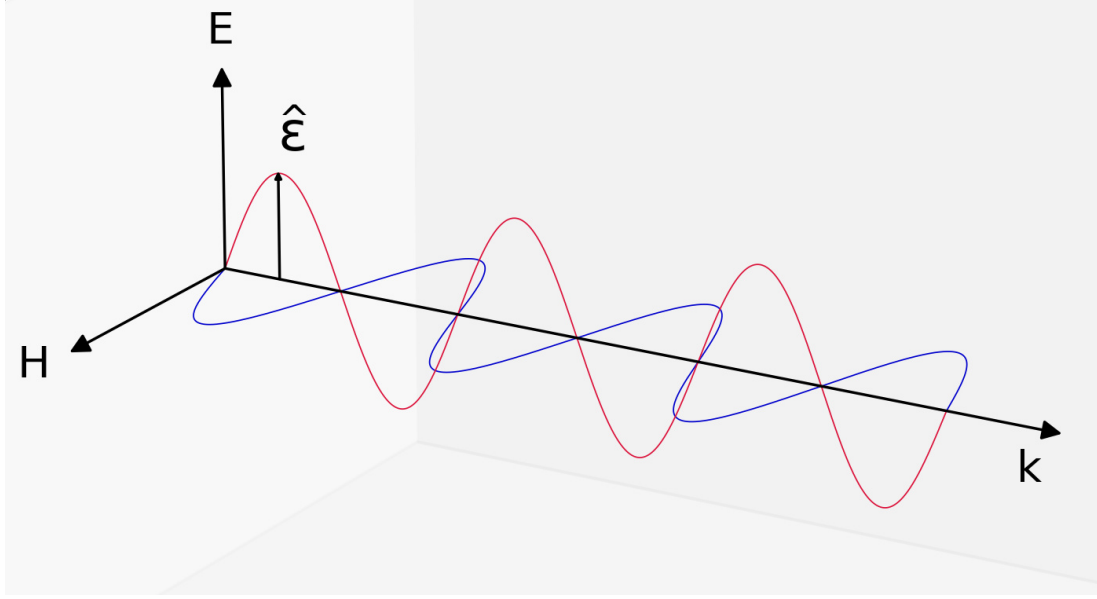


Figure 2.1.: An X-ray is a transverse electromagnetic wave. Its electric and magnetic fields, $\mathbf{E}$ and $\mathbf{H}$, are perpendicular to each other, and to the direction of propagation $\mathbf{k}$. The direction of the electric field is determined by the polarization unit vector $\hat{\epsilon}$. Illustration adapted from [45].

or molecules, it may be more convenient to consider the material as a continuum, with an interface to the adjacent vacuum (or air). At the interface, the X-ray beam experiences both refraction and reflection, thus establishing another way in which the interaction can occur.

2.1.2. Classical scattering experiment[†]

From the classical perspective of the elementary scattering event, the electric field of the incident X-rays exerts a force on the electronic charge, which in turn accelerates and radiates the scattered wave. When the wavelength of the scattered wave is the same as that of the incident one, the scattering is necessarily *elastic*. This statement is not universally valid in the context of quantum mechanics. In this case the incoming X-ray photon has a momentum of $\hbar\mathbf{k}$ and an energy of $\hbar\omega$. The electron may gain energy, resulting in the scattered photon possessing a frequency lower than that of the incident one. This *inelastic* scattering process is known as the Compton effect and is outside the scope of the present thesis. The elastic scattering of X-rays is typically used to study the structure of materials. For this purpose, a classical approach is sufficient.

The cross-section holds significance as it serves as the point where empirical observation and theoretical prediction converge. A schematic of a generic scattering experiment on a single, free electron, is displayed in Fig. 2.2. The fundamental quantity established in

[†]Most of the contents of this paragraph are adapted from the book [45]. Other references are indicated.

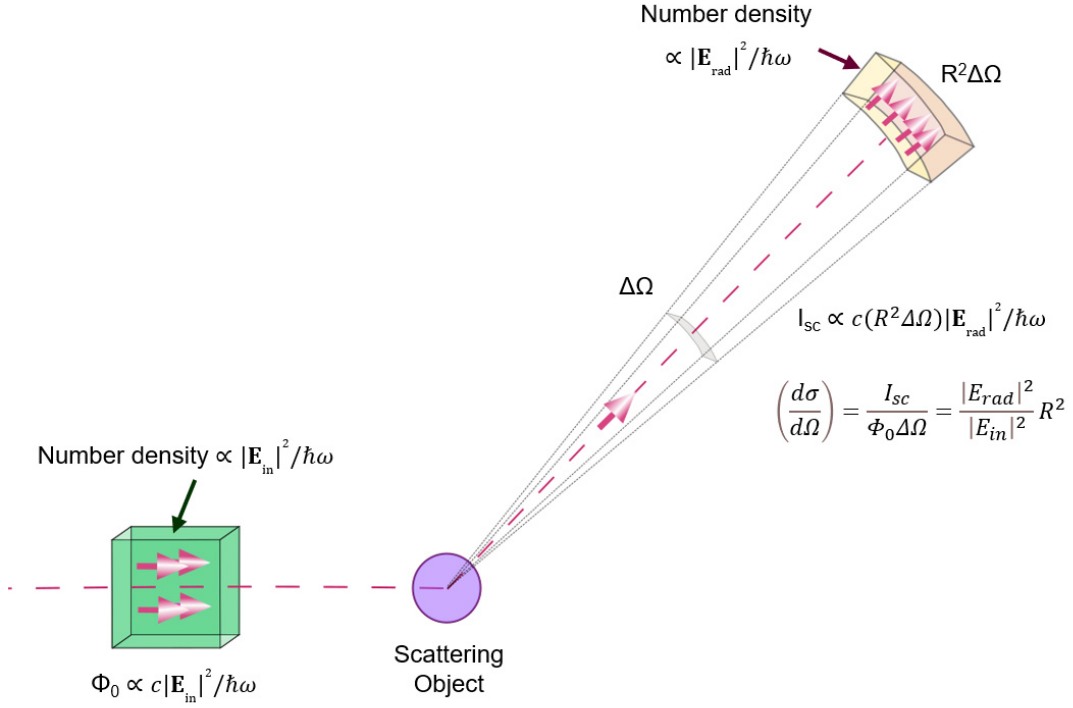


Figure 2.2.: Schematic layout of a generic scattering experiment used to determine the differential cross-section ($d\sigma/d\Omega$): see Eq. (2.3). The incident beam flux Φ_0 is the number of particles per second per unit area. For an electromagnetic wave this is proportional to $|\mathbf{E}_{in}|^2$ times the velocity of light, c . The incident beam interacts with the target object to produce the scattered beam. A detector records the scattered intensity, I_{sc} , defined as the number of counts recorded per second, which is proportional to $|\mathbf{E}_{rad}|^2$ times the area of the detector and the velocity of light. The detector is located a distance R from the target object, and subtends a solid angle of $\Delta\Omega$. Illustration adapted from [45].

such an experiment is the *differential scattering cross-section* which is defined as follows:

$$\frac{d\sigma}{d\Omega} = \frac{I_{sc}}{\Phi_0 \Delta\Omega} \quad (2.3)$$

The strength of the incident beam is determined by its flux, Φ_0 , which is the number of photons passing through a unit area in one second. The scattering object interacts with the incident beam and causes it to be scattered. The rate of photons scattered per second by an object, detected at a distance R and within a specific solid angle $\Delta\Omega$, is recorded as I_{sc} . This represents the scattering efficiency of the process and is quantified by the differential cross-section where details of the experiment, such as specifically the flux of the incident beam and size of the detector, have been normalized away.

For an object, which is larger than the size of an X-ray beam of intensity I_0 photons per

second, the scattering event is shown in Fig. 2.3. The measure of interest is the quantity of X-ray photons, I_{sc} , that scatter into a detector per second, subtending a solid angle $\Delta\Omega$. For N particles in the sample per unit area seen along the beam direction, the intensity of the scattered beam I_{sc} will be proportional to N , I_0 and $\Delta\Omega$. In addition, the efficiency with which the particles in the sample scatter the radiation will have an impact on the detected I_{sc} . The differential cross-section per scattering particle is defined by:

$$\frac{d\sigma}{d\Omega} = \frac{\text{No. of X-ray photons scattered per second into } \Delta\Omega}{I_0 N \Delta\Omega} \quad (2.4)$$

For the situation when the beam is larger than the sample, the incident *flux* of X-rays is considered, which is essentially a number of photons per second per unit area. Then, the scattering intensity can be calculated as:

$$I_{sc} = \Phi_0 \Delta\Omega \left(\frac{d\sigma}{d\Omega} \right), \quad (2.5)$$

where Φ_0 is the flux of the incident beam, while differential cross-section refers to the irradiated sample. In current work, both situations are possible, since for scattering experiments with grazing incidence geometry the X-ray beam might not irradiate the complete sample of interest. This feature will be discussed further, as it is commonly used as surface-sensitive technique which allows for obtaining the information about phase composition depending on the penetration depth of the X-rays.

For the scattering event of an electromagnetic wave displayed in Fig. 2.2, flux Φ_0 can

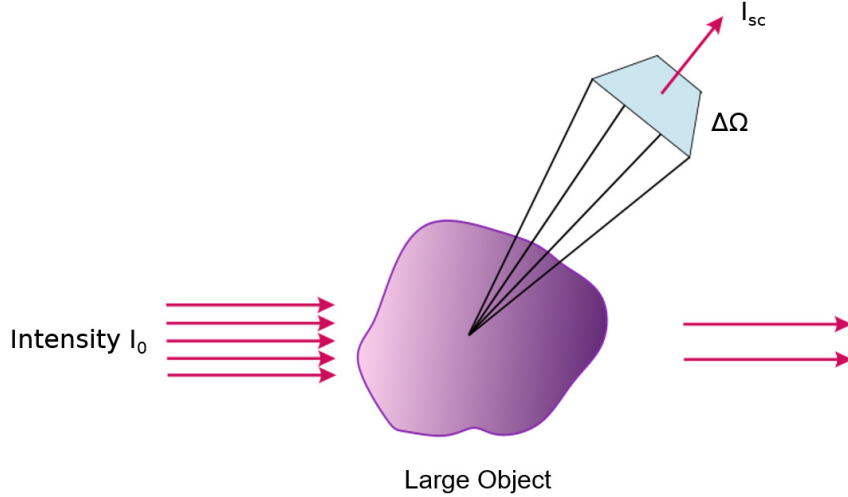


Figure 2.3.: A beam is incident on a sample with a larger cross-sectional area. In this case the intensity I_{sc} scattered into a solid angle $\Delta\Omega$ is proportional to the incident *intensity* I_0 of the beam, i.e. the number of photons per second. Illustration adapted from [45].

be expressed in terms of the electrical field $\mathbf{E}_{in}$ of the incident beam. The energy density

is proportional to $|\mathbf{E}_{in}|$, while the flux Φ_0 is the number density of photons, which is proportional to $|\mathbf{E}_{in}|^2/\hbar\omega$, times speed of light, c . The intensity of the scattered beam I_{sc} is in turn proportional to $|\mathbf{E}_{rad}|^2$ multiplied by the detector area, which is expressed as $R^2\Delta\Omega$, and speed of light c . Then, the differential cross-section is expressed as:

$$\frac{d\sigma}{d\Omega} = \frac{|\mathbf{E}_{rad}|^2 R^2}{|\mathbf{E}_{in}|^2} \quad (2.6)$$

In the frame of a classical description of the scattering process, an electron will be forced to vibrate when placed in the electric field of an incoming X-ray beam. An electron acts as a source and radiates a spherical wave $\mathbf{E}_{rad}\hat{\boldsymbol{\epsilon}}'e^{ikR}/R$. The radiated field at the observation point X will be discussed for the case where X lies in the plane spanned by the polarization vector and the propagation direction of the incident wave and at an angle of $90^\circ - \Psi$ with respect to the direction of the propagation of the incident beam.

The radiated field is then proportional to the charge of the electron, $-e$, and to the acceleration $a_X(t')$ evaluated at time t' earlier than the observation time t due to the finite speed c at which the radiation propagates. The radiated field then can be expressed as:

$$E_{rad}(R, t) \propto \frac{-e}{R} a_x(t') \sin\Psi \quad (2.7)$$

where $t' = t - R/c$. The full acceleration can be evaluated from the force on the electron divided by its mass, which leads to:

$$a_x(t') = \frac{-eE_0e^{-i\omega t'}}{m} = \frac{-e}{m} E_{in}e^{i\omega(R/c)} = \frac{-e}{m} E_{in}e^{ikR} \quad (2.8)$$

where $E_{in} = E_0E^{-i\omega t}$ is the electric field of the incident wave. As a result, the relation for cross-section evaluation can be expressed as:

$$\frac{E_{rad}(R, t)}{E_{in}} \propto \left(\frac{e^2}{m}\right) \frac{e^{ikR}}{R} \sin\Psi \quad (2.9)$$

For an observation point at an arbitrary angle with respect to the polarization of the incident beam, the factor of $\sin\Psi$ must be reevaluated. If $\hat{\boldsymbol{\epsilon}}$ is the polarization of the incident field, and $\hat{\boldsymbol{\epsilon}}'$ that of the radiated field, then $\hat{\boldsymbol{\epsilon}} \cdot \hat{\boldsymbol{\epsilon}}' = \cos(90^\circ + \Psi) = -\sin(\Psi)$.

In order to complete the derivation of the differential cross-section, one can note that in SI units the Coulomb energy at distance r from a point charge $-e$ is $e^2/(4\pi\epsilon_0 r)$, while dimensionally the energy is also of the form mc^2 . Therefore, the fundamental length in the problem is:

$$r_e = \left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right) = 2.82 \times 10^{-5} \text{ \AA} \quad (2.10)$$

By definition, this is the Thomson scattering length, or classical radius, of an electron. The scattering amplitude from a single electron is equal to $-r_e|\hat{\boldsymbol{\epsilon}} \cdot \hat{\boldsymbol{\epsilon}}'|$. Physically, the factor of -1 represents the presence of a 180° phase shift between the incident and scattered waves.

This phase shift also has consequences for the refractive index n which in the X-ray region is less than unity, as it will be discussed further.

The ratio of radiated to incident electric field is then expressed as:

$$\frac{E_{rad}(R, t)}{E_{in}} = -r_e \frac{e^{ikR}}{R} |\hat{\epsilon} \cdot \hat{\epsilon}'| \quad (2.11)$$

and the differential cross-section becomes:

$$\left(\frac{d\sigma}{d\Omega}\right) = r_0^2 |\hat{\epsilon} \cdot \hat{\epsilon}'|^2 \quad (2.12)$$

This equation describes the Thomson differential cross-section of an electromagnetic wave by a free electron. The factor of $|\hat{\epsilon} \cdot \hat{\epsilon}'|^2$ influences the choice of optimal geometry for different types of X-ray experiments. In particular, synchrotron sources naturally produce X-rays which are linearly polarized in the horizontal plane of the synchrotron. The polarization factor for scattering P can be defined depending on the X-ray source:

$$P = |\hat{\epsilon} \cdot \hat{\epsilon}'|^2 = \begin{cases} 1 & \text{synchrotron: vertical scattering plane} \\ \cos^2\psi & \text{synchrotron: horizontal scattering plane} \\ \frac{1}{2}(1 + \cos^2\psi) & \text{unpolarized source} \end{cases} \quad (2.13)$$

As a result, the scattering experiments at synchrotron are best performed in a vertical scattering plane, since $|\hat{\epsilon} \cdot \hat{\epsilon}'|^2 = 1$ independent of the scattering angle, which is defined as $\psi = 90^\circ - \Psi$. On the other hand, for studying fluorescence from the sample, one can suppress the scattering by working in the horizontal plane at $\psi = 90^\circ$ since $|\hat{\epsilon} \cdot \hat{\epsilon}'|^2 = 0$

2.1.3. Scattering from one atom, one molecule and a crystal[‡]

According to a purely classical description, the electron distribution is specified by a number density, $\rho(\mathbf{r})$. Contributions from different volume elements of this charge distribution combine to form the scattered radiation field. To assess this combination, it is necessary to note the phase of the incident wave as it interacts with the volume element at the origin and the one at position $\mathbf{r}$, depicted in Fig. 2.4(a). The phase difference between two successive crests is 2π . The phase difference between the two volume elements can be calculated by multiplying 2π with the ratio of $\mathbf{r}$, projected onto the incident direction, and the wavelength. This is simply the scalar product of the two vectors $\mathbf{k}$ and $\mathbf{r}$. The phase difference between the scattered wave from a volume element around the origin and one around $\mathbf{k}$ is $-\mathbf{k}' \cdot \mathbf{r}$. Therefore, the resulting phase difference is expressed as:

$$\Delta\phi \cdot \mathbf{r} = (\mathbf{k} - \mathbf{k}') \cdot \mathbf{r} = \mathbf{q} \cdot \mathbf{r} \quad (2.14)$$

[‡]Most of the contents of this paragraph are adapted from the book [45]. Other references are indicated.

where the value $\mathbf{q}$ is known as the *scattering vector*:

$$\mathbf{q} = \mathbf{k} - \mathbf{k}' \quad (2.15)$$

For elastic scattering events, displayed in Fig. 2.4(a), $|\mathbf{k}| = |\mathbf{k}'|$, the scattering triangle results in $|\mathbf{q}| = 2|\mathbf{k}|\sin\theta = (4\pi/\lambda)\sin\theta$. As a result, $\mathbf{q}$ is the most appropriate quantity to describe elastic scattering processes and is commonly expressed in units of $\text{\AA}^{-1}$.

Therefore, for an atom, a volume element $d\mathbf{r}$ at $\mathbf{r}$ will give a contribution of $-r_0\rho(\mathbf{r})d\mathbf{r}$

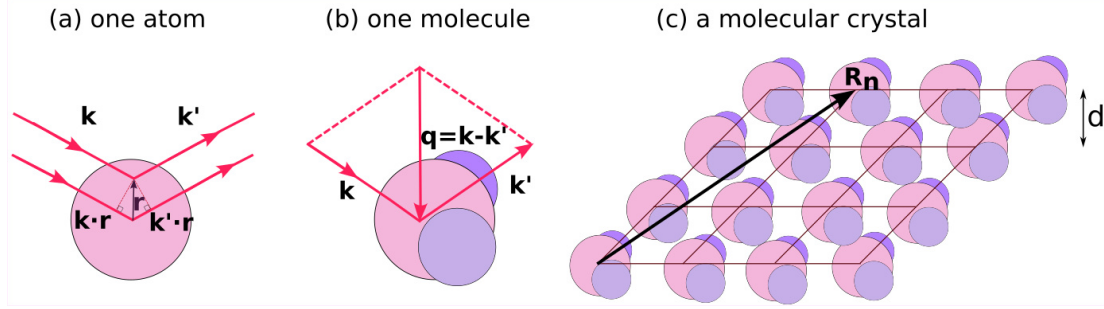


Figure 2.4.: (a) Scattering from an atom. An X-ray with a wave vector $\mathbf{k}$ scatters from an atom to the direction specified by $\mathbf{k}'$. The scattering is assumed to be elastic, i.e. $|\mathbf{k}| = |\mathbf{k}'| = 2\pi/\lambda$. The difference in phase between a wave scattered at the origin and one at a position $\mathbf{r}$ is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r} = \mathbf{q} \cdot \mathbf{r}$. This defines the wave vector transfer $\mathbf{q}$. (b) Scattering from a molecule. Here the scattering triangle is shown which $\mathbf{k}$, $\mathbf{k}'$ and $\mathbf{q}$. (c) Scattering from a molecular crystal. The molecules are organized on a lattice with position vectors $\mathbf{R}_n$, and a lattice plane spacing of d . Illustration adapted from [45].

along with a phase factor of $e^{i\mathbf{q} \cdot \mathbf{r}}$. As a result, the totalling scattering length of an atom can be written as:

$$-r_0 f^0(\mathbf{q}) = -r_0 \int \rho(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} \quad (2.16)$$

where $f^0(\mathbf{q})$ is the *atomic form factor*. In the limit that $\mathbf{q} \rightarrow 0$ all the volume elements scatter in phase so that $f^0(\mathbf{q} = 0) = Z$, which is the number of electrons in the atom. The scattering length can be precisely calculated from the Fourier transform of the distribution of electrons in the sample.

When studying more complex system, such as a molecule composed of atoms, displayed in Fig. 2.4(b), its scattering length will also have a form factor. Labelling each atom in the molecule by its index, j , yields the expression:

$$F^{mol}(\mathbf{q}) = \sum_j f_j(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_j} \quad (2.17)$$

where $f_j(\mathbf{q})$ is the atomic form factor of the j^{th} atom in the molecule.

The crystalline material is periodic in space (Fig. 2.4(c)), therefore it is important to specify a position of each atom within the crystal. If $\mathbf{R}_n$ are the lattice vectors which

define the lattice within the studied crystal, and $\mathbf{r}_j$ defines the position of the atoms relative to any specific lattice site, then the position of any atom in the crystal is $\mathbf{R}_n + \mathbf{r}_j$. Consequently, the scattering amplitude for the crystal is factorised into two terms, written as:

$$F^{crystal}(\mathbf{q}) = \overbrace{\sum_j f_j(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_j}}^{\text{Unit cell structure factor}} \cdot \overbrace{\sum_n e^{i\mathbf{q} \cdot \mathbf{R}_n}}^{\text{Lattice sum}} \quad (2.18)$$

the first term is the *unit cell structure factor*, while the second term is a sum over lattice sites. In applications like solid state physics and thin film characterization the structure of the material is of interest on its own, while for molecular and protein crystallography, assembling the molecules on a lattice is used to amplify the scattering signal.

2.1.4. Derivation of the Bragg's law[§]

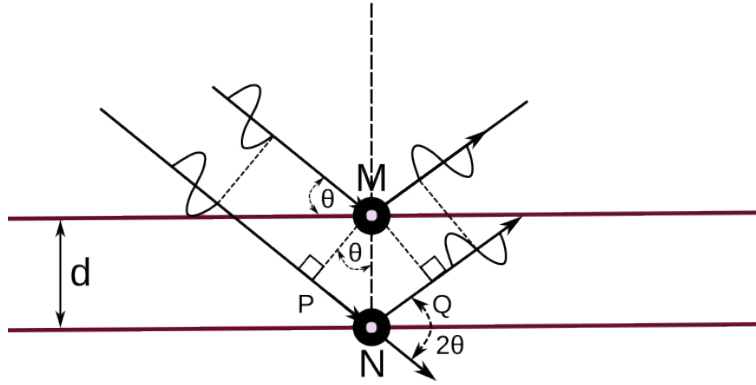


Figure 2.5.: Illustration of the geometry utilized for the simplified derivation of Bragg's law. Illustration adapted from [47].

The simplest way to obtain structural information from powder diffraction is to use the well-known Bragg equation (W.L. Bragg, 1912), which describes the principle of X-ray diffraction by scattering of X-rays off sets of lattice planes. The crystallographic planes, known as lattice planes, are identified by the Miller indices hkl , a triplet of the integer indices. Parallel planes with identical indices are equally spaced and separated by the distance d_{hkl} . Bragg analysis treats X-rays like visible light being reflected by the surface of a mirror, with the X-rays being specularly reflected at the lattice planes. In contrast to visible light of lower energy, X-rays penetrate deeply into materials, causing additional reflections at thousands of consecutively parallel planes. Due to their uniform direction of reflection, the scattered X-rays undergo superposition. Based on Fig. 2.5, it is evident that the second wave travels a longer distance PN prior to and NQ subsequent to reflection. Constructive interference occurs only if $\Delta = PN + NQ$ is a multiple $n = 0, \pm 1, \pm 2, \dots$ of

[§]Most of the contents of this paragraph are adapted from the chapter [47]. Other references are indicated.

the wavelength λ :

$$\Delta = n\lambda \quad (2.19)$$

In all other cases, destructive interference occurs, since it is possible to find a lower plane, p , which satisfies the equation $p\Delta = n\lambda$ with $n = \pm 1/2, \pm 3/2, \dots$ (in other words, perfect destructive interference). As illustrated in Fig. 2.5, mathematically, the interplanar spacing of parallel lattice planes (d) and the diffraction angle (2θ) between incoming and outgoing X-ray beams can be employed to calculate Δ geometrically *via* the formula:

$$\Delta = 2d \sin(\theta) \quad (2.20)$$

The Bragg law can be derived by combining the preceding two equations:

$$n\lambda = 2d \sin(\theta) \quad (2.21)$$

This is a useful construction, but it has its limitations. The main one is that it does not allow us to calculate the intensity of the scattering for which there is constructive interference. For that, it is important to derive the scattering amplitude of the crystal.

2.1.5. Grazing incidence geometry[¶]

X-ray diffraction is one of the most important techniques to investigate structures at the nanoscale. While a single crystal has a 'perfect' three-dimensional lattice, powders and films typically demonstrate differing levels of ordered and preferred orientations. The grazing incidence geometry is characterized by a low incidence angle ($\alpha_i = 0-1^\circ$) which is defined as the angle between the incoming X-ray beam and the sample surface. X-rays have an index of refraction $n = 1 - \delta + i\beta$, where δ is on the order of 10^{-6} , while the imaginary term with $\beta \simeq 10^{-8}$ accounts for absorption. The δ and β can be calculated based on the wavelength, stoichiometry of the material, and its density. The Grazing-Incidence X-ray Diffraction (GIXD) method is widely recognized for the deep insight it provides into the structure of interfaces, surfaces, and films [49]. When the incidence angle α_i is smaller than the critical angle α_c , a total external reflection of the X-ray beam occurs, i.e. the only rapidly decaying evanescent beam probes the sample interior. The notable feature of GIXD is its ability to facilitate the examination of thin films on substrates. The thin film profile can be accessed through GIXD measurements by adjusting the angle of incidence to control the penetration depth of the X-ray beam [30], as displayed in Fig. 2.6. The bulk signal is strongly suppressed, resulting in a significant improvement in the signal-to-noise ratio with respect to scattering from the surface layers of a few nanometers in thickness (Fig. 2.6(a)). By increasing the angle of incidence close to or slightly above the critical angle, the crystal structure of the film can be measured at a certain depth due to the partial penetration of X-rays. The probing depth (the depth at which the magnitude of

[¶]Most of the contents of this paragraph are adapted from the article [48]. Other references are indicated.

the X-ray beam is attenuated by $1/e$) in the limit of $\alpha_i \rightarrow 0$ can be estimated by the following formula [50]:

$$\Lambda_0 = \lambda / (2\pi\alpha_c) \quad (2.22)$$

where λ is the wavelength of the probing X-ray beam. The critical angle α_c is calculated *via* the formula:

$$\alpha_c = \lambda \sqrt{\frac{r_e \rho}{\pi}} \quad (2.23)$$

where r_e is the Thomson scattering length of the electron ($=2.817 \times 10^{-5} \text{ \AA}$) and ρ is the electron density of the film material.

The estimated X-ray penetration depth for a typical X-ray laboratory source ($\lambda =$

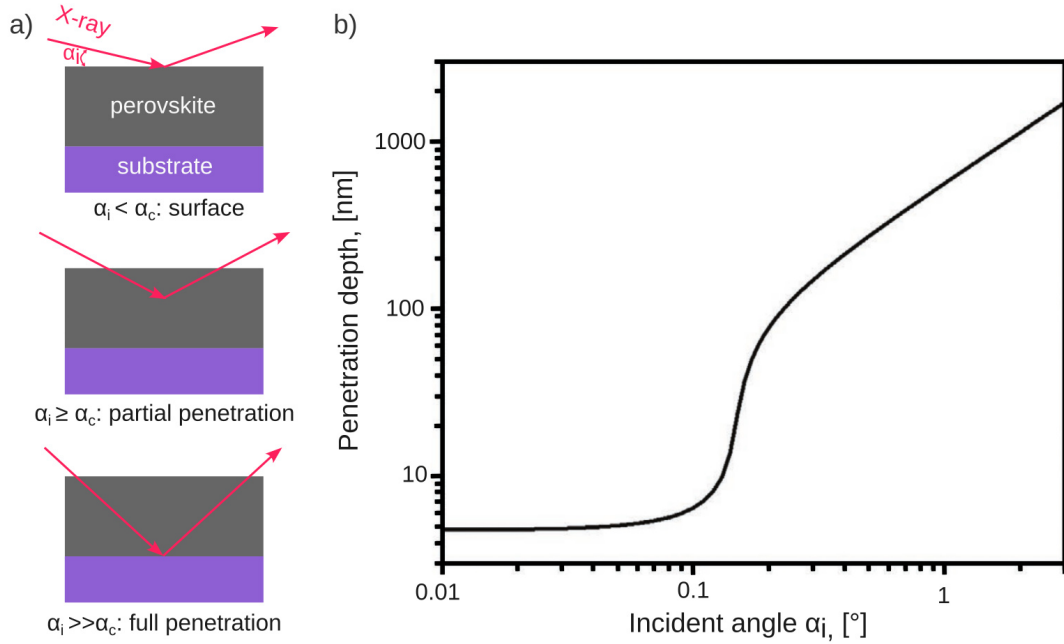


Figure 2.6.: (a) Schematics of the dependence of X-ray penetration depth on the incident angle α_i and the critical angle α_c . b) The estimated X-ray penetration depth in a typical 3D perovskite film[51]; the X-ray wavelength $\lambda = 1.54 \text{ \AA}$. Illustration adapted from [30].

$1.54 \text{ \AA}$), including absorption-related correction β_n in 3D perovskite, an excessively studied material in the present work, is displayed in Fig. 2.6(c). When a crystalline material is studied, the integrated scattering intensity of each crystalline-phase reflection is proportional to the irradiated volume of the phase. In addition to that, quantitative information on the thickness of thin polycrystalline layers can be obtained from GIXD scans [52]. This calculation can be performed once the film density is properly known, for example, for thick films, when in general the bulk mass density can be assumed. Full penetration of X-rays into the bulk of the film can be achieved by progressively increasing the angle of incidence until substrate signals are observed, which in turn probe the average structural

information across the film. On the basis of X-ray scattering spectra, collected at different angles of incidence, structural information can be obtained at different depths of the film [52]. Grazing incidence X-ray scattering methods reveal microstructure features including crystal structure, polymorphism, grain size and mosaicity, preferential orientation, in-plane texture and grain boundaries [6, 53].

GIXD is a powerful surface scattering technique; however, there is a more modern

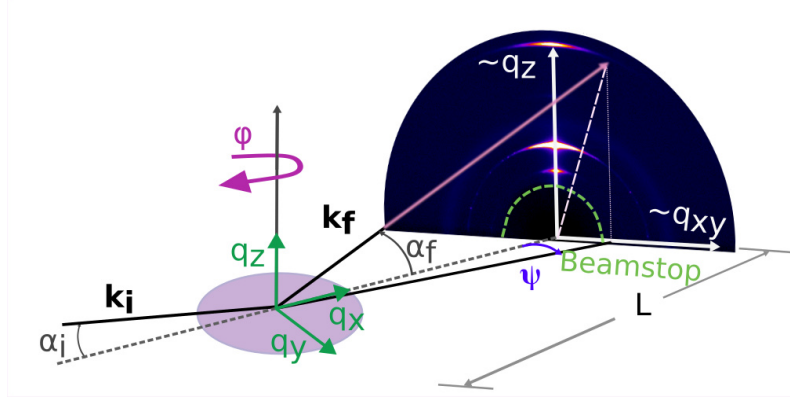


Figure 2.7.: Scattering geometry of GIWAXS. The incident beam of the wave vector $\mathbf{k}_i$ hits the sample with a shallow incident angle of α_i , producing a scattered wave $\mathbf{k}_f$ with respect to the sample surface. The outgoing plane has an azimuthal angle ψ with respect to the incident beam plane. The direct beam points to the origin of the reciprocal space [30]. Grazing incidence geometry corresponds to angle of incidence $\alpha = 0-1^\circ$.

method to probe the structure of thin films on the molecular scale, GIWAXS, which utilizes a 2D detector instead of a point detector [54]. GIWAXS measurements collect diffuse scattering with an area detector, while in GIXD higher resolution scans using point or line detector are performed. The use of collimation (using special collimating slits or Soller collimators) [55] significantly changes the resolution function. The present thesis includes only two GIXD datasets with increased resolution (due to the use of a point detector), while the majority of data is *in situ* GIWAXS, displaying the formation and growth of thin films of interest.

The measuring configuration of the GIWAXS technique is shown in Fig. 2.7. An X-ray beam with the incoming vector $\mathbf{k}_i$ is directed at the sample surface under a grazing incidence angle of α_i , and the scattered wave $\mathbf{k}_f$ is collected by a 2D area detector. The scattering angle 2θ is measured from the direction of the incoming beam to the direction of the observation of the scattered beam. The scattering wave vector $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ is then expressed in the following components [56]:

$$q_x = \frac{2\pi}{\lambda}(\cos \alpha_f \cos \psi - \cos \alpha_i) \quad (2.24)$$

$$q_y = \frac{2\pi}{\lambda}(\cos \alpha_f \sin \psi) \quad (2.25)$$

$$q_z = \frac{2\pi}{\lambda}(\sin \alpha_i + \sin \alpha_f) \quad (2.26)$$

$$q_r = \sqrt{q_x^2 + q_y^2} \quad (2.27)$$

where q_z is along out-of-plane direction with respect to the sample surface, while q_x and q_y being in the in-plane direction, being parallel and perpendicular to the incident plane, respectively. The image on the 2D detector in Fig. 2.7(d) has to be converted into the reciprocal space associated with the sample, which reveals the existence of the inaccessible region, or the so-called "missing wedge" in the GIWAXS pattern presented in Fig. 2.8 owing to the curvature of the Ewald sphere [57]. As illustrated in Fig. 2.8(a), diffraction signals originating from highly oriented crystallites are hidden in the inaccessible zone. X-ray scattering from thin films includes information on the orientation of crystallites in the sample [58]. Thin films often exhibit preferred orientation of the domains/crystallites, which is also referred to as texture of the samples. This might result in a misleading nature of the one-dimensional or line scan, such as conventional GIXD, which does not account for crystallites oriented out of plane. Therefore, combining 2D GIWAXS scattering patterns (with a "missing wedge" as displayed in Fig. 2.8(b)) and measuring the specular reflection along the q_z axis with X-ray reflectivity (XRR) is a way to access the whole Ewald sphere.

GIWAXS measurements can be used for the estimation of the coherently scattering crystallite size within thin films, since this property causes peak broadening. However, it is important to consider all intrinsic and extrinsic factors, besides crystallite size, which are able to contribute into the Bragg peak broadening [58]. The intrinsic phenomena include various structural defects (e.g., twins, dislocations, stacking faults), chemical heterogeneity of solid solutions and microscopic stress [59]. In some cases, the broadening caused by the solid solution structure is dominant, as the optoelectronic properties are tuned by alloying such materials [60]. The instrumental broadening of the setup can be estimated from a well-defined powder sample, such as the National Institute of Standards and Technology (NIST) LaB_6 standard, which has a negligible sample broadening [8]. For Gaussian-type peaks, the full width at half maximum (FWHM) of each peak in the experimental GIWAXS profile (FWHM_{exp}) yields both instrumental broadening (FWHM_{inst}) and sample broadening (FWHM_{sam}) via:

$$\text{FWHM}_{exp} = \sqrt{\text{FWHM}_{inst}^2 + \text{FWHM}_{sam}^2}. \quad (2.28)$$

The Scherrer's equation relates the FWHM_{hkl} of a diffraction spot with (hkl) Miller indices to the average grain size D_{hkl} of the material of interest:

$$D_{hkl} = \frac{K\lambda}{\text{FWHM}_{hkl} \cos(\theta_{hkl})}, \quad (2.29)$$

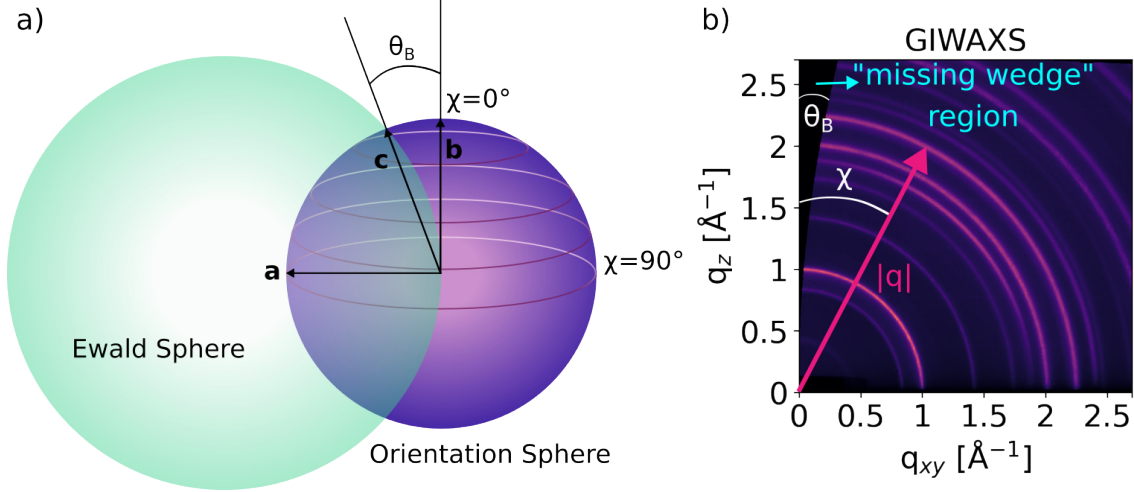


Figure 2.8.: a) Intersection of Ewald sphere with crystallite orientation sphere, indicating possible diffraction events in grazing incidence geometry. **a** is the vector denoting an in-plane reciprocal lattice vector that results in pure horizontal scattering ($\chi = 90^\circ$), **b** is the vector denoting an out-of-plane reciprocal lattice vector ($\chi = 0^\circ$), which in the grazing-incidence geometry does not result in any observable scattering, and **c** is the vector denoting off-vertical reciprocal lattice vector which results in pure vertical scattering in the grazing incidence diffraction geometry. The local-specular condition is met when the substrate (and therefore orientation sphere) is tilted at θ_B . b) The polar angle χ is the angle between the q_z axis and the projection of the scattering wave vector $\mathbf{q}$ on the $q_r - q_z$ plane, while the polar angle θ_B corresponds to the minimum detectable χ . Illustration adapted from [30, 57].

where the X-ray wavelength is denoted as λ and the Bragg angle is θ_{hkl} . K is the Scherrer constant, which has a value of about 0.9, since it can be derived as $K = 2[2 \ln(2)/\pi] \simeq 0.93$ [54].

A more modern representation is made in reciprocal space:

$$\Delta q_{hkl} = \frac{4\pi}{\lambda} \cos(\theta_{hkl}) \frac{\text{FWHM}_{hkl}}{2}, \quad (2.30)$$

where $\text{FWHM}_{hkl} = \Delta(2\theta_{hkl})$ is defined by the width of the Bragg peak. which leads to the following formula:

$$D_{hkl} = 2\pi K / \Delta q_{hkl}. \quad (2.31)$$

Strain effects are pronounced in inorganic thin films (hard matter), while soft materials are adaptable and rather deform (create defects or grain boundaries) than build up extended strain fields [54]. Soft materials may display only a few diffraction orders because of the absence of true long-range order. However, the FWHM of the lowest-order reflections, where the impact of additional intrinsic broadening effects is the least pronounced, will fully provide a valuable estimation of the average grain size. In general, with all assumptions for instrumental and non-instrumental factors, Scherrer's equation can only

be applied for average sizes of up to 100-200 nm (depending on the signal-to-noise ratio, sample, and the chosen X-ray method) [61]. Another way to extract information on the lattice strain and crystallite size is Williamson–Hall method [62]. This method is more precise due to its ability to account for the presence of strain, uniform or non-uniform, and discriminate between the impacts of the strain and the size of the crystallite on FWHM. The peak width derived from the crystallite size varies as $1/\cos\theta$, while the strain varies as $\tan\theta$.

2.1.6. X-Ray Reflectivity

X-ray reflectivity (XRR) is a non-destructive technique commonly used to estimate the thickness of homogeneous, flat, and smooth layers in single- and multilayer thin films, with thicknesses below a few hundred nanometers [52]. The main idea of XRR measurements is that careful choice of the scattering vector, defined by the specular geometry, the scattering length density (SLD) profile can be studied, representing the electron density distribution $\rho_e(z)$ along the sample surface normal, as well as the roughness of the interface of thin films [63]. The experimental setup for the specular reflectivity measurements is presented in Fig. 2.9 [64]. The sample on the diffractometer is illuminated with collimated monochromatic radiation at an angle of incidence θ , while the reflected beam is measured at the same exit angle θ . The specular condition then ensures that q_z is always perpendicular to the sample. Typically, each measurement is performed over a range of angles and q_z values, and in the current work it is complementary to the *ex situ* GIWAXS measurements, since some of the essential scattering features are located in the "missing wedge", displayed in Fig. 2.8.

The incoming X-ray beam is reflected by single atoms and molecules, since they have electrons that cause scattering, the presence of interfaces induces additional features, corresponding to nanometer and micrometer-scale structures in addition to Bragg reflections [45]. A typical XRR measurement of an organic film on a silicon substrate is displayed in Fig. 2.10. For this work, the most essential features of the data are the Kiessig fringes, which relate to the thickness and roughness of the film, and the position of the total reflection edge (TRE), which relates to SLD. It allows us to estimate the SLD profile along the surface normal of some 2D perovskite samples, which reflects the thickness of the thin film and the roughness of the interface.

The complete analysis of this kind of data requires careful mathematical modeling, which can be found elsewhere [45]. In the current work, it is used mainly for qualitative analysis of the resulting thin films and to compare the effects of different organic and inorganic compounds on the quality and roughness of thin films.

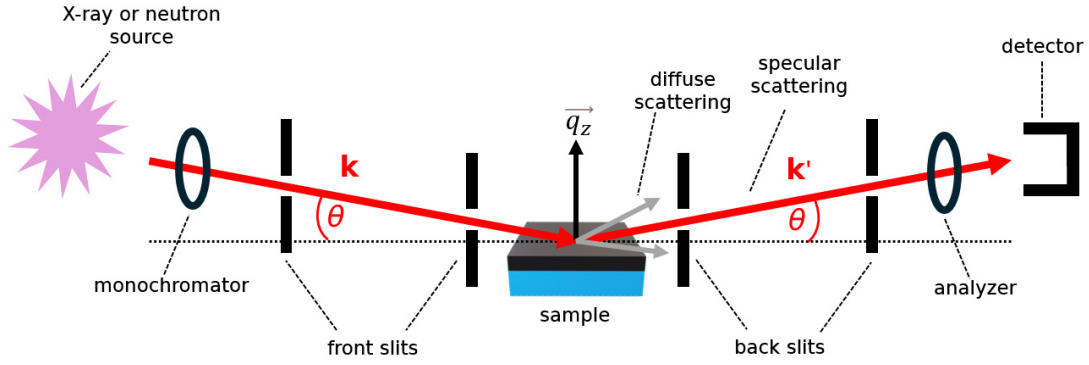


Figure 2.9.: Typical experimental setup for specular reflectivity measurements. An incident beam of neutrons or X-rays impinges on the sample at an incident angle θ and the specular reflection (at the same outgoing angle θ). To ensure the specular condition, both the incoming and outgoing beam are collimated *via* a pair of slits and passed through a monochromator and analyzer, respectively. This results in a moment transfer vector $\vec{q}_z$ perpendicular to the sample surface for the measured signal. Each measurement is typically performed over a range of q_z values. Adapted from [64].

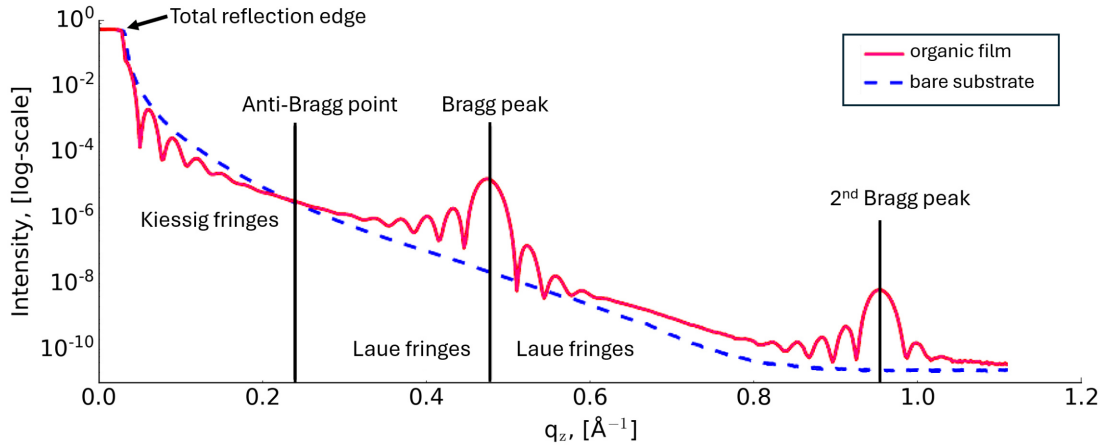


Figure 2.10.: Example of a typical reflectivity measurement of an organic thin film on a silicon substrate. The most important features with respect to this thesis are the Kiessig fringes and the TRE. The periodicity and decay of the Kiessig fringes yield information about the thickness and roughness of the film, respectively. The position of the TRE is given by the critical angle and thus related to the SLD. Adapted from [65].

2.2. X-ray scattering on perovskite materials

The present section is focused on the features of using X-ray scattering methods for studying perovskite growth kinetics and their structural properties. In particular, it shows a signature pattern that can be observed within the GIWAXS data that might hint towards the structure of the sample studied. X-ray scattering methods are commonly used to study the formation of a perovskite phase within different compositions *in situ* [8, 28,

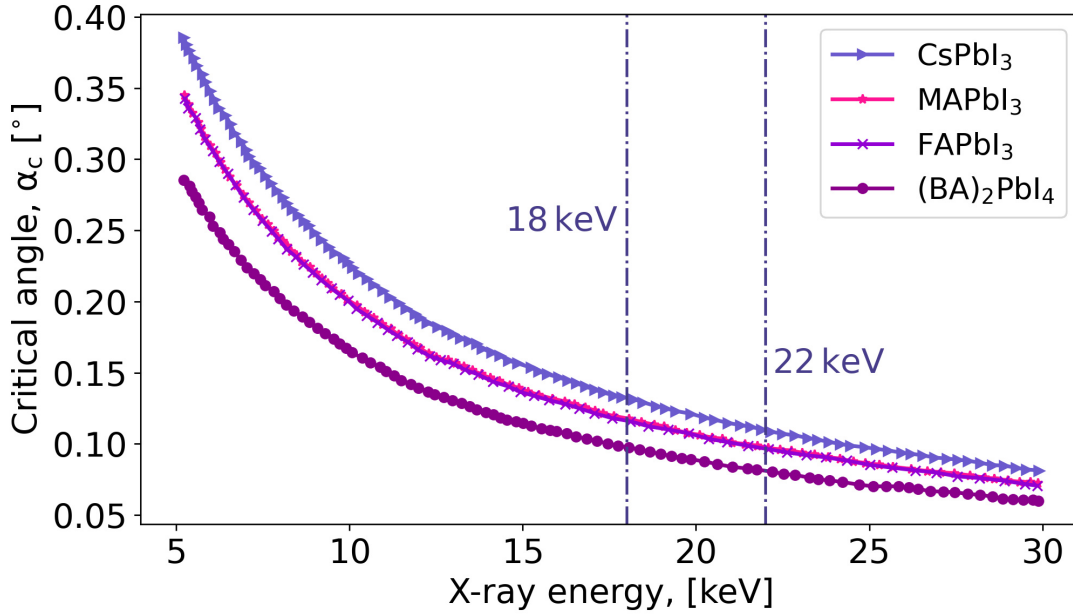


Figure 2.11.: Critical angles of relevant metal halide perovskite materials at room temperature, as a function of the GIWAXS X-ray energy. For a 2D perovskite composition, namely $(\text{BA})_2\text{PbI}_4$, critical angles are lower than for 3D perovskite compositions (all other curves). Vertical dash-dotted lines indicate the X-ray beam energies: 18 keV and 22 keV, used for *in situ* and *ex situ* X-ray scattering experiments, presented in current thesis. Adapted from [8].

[66–68] and to test the stability of the perovskite film within a solar cell *in operando* [67, 69, 70]. Various processes and characteristics can be studied within the films, such as: liquid-to-solid transformation mechanisms *via* intermediate phases [67, 71], the influence of precursor solutions used to produce perovskites [31], the crystallization dynamics under different conditions [72] and microstructure evolution [73]. The phase distribution within the final film is probed by GIWAXS with varying angle of incidence, which provides the penetration depth-dependent scattering profile, including information about the surface layer (below critical angle) and the whole perovskite thin film (above critical angle). The critical angles for different relevant perovskite compositions, depending on the X-ray energy, are displayed in Fig. 2.11.

In situ X-ray scattering experiments under air atmosphere might destroy some perovskite phase components, which then leads to its decrease in scattering intensity and the formation of PbI_2 [58]. The high-energy beam causes unavoidable damage to perovskite materials because of its sensitivity and nature. The measurement conditions should be precisely controlled in order to eliminate the damage and artifacts, otherwise a degradation mechanism can be triggered. More accurate experimental results can be obtained with synchrotron X-ray radiation to track crystallization *in situ* [74].

There are various signatures which are common for different oriented structural motifs depending on the degrees of ordering and their orientation relative to the substrate.

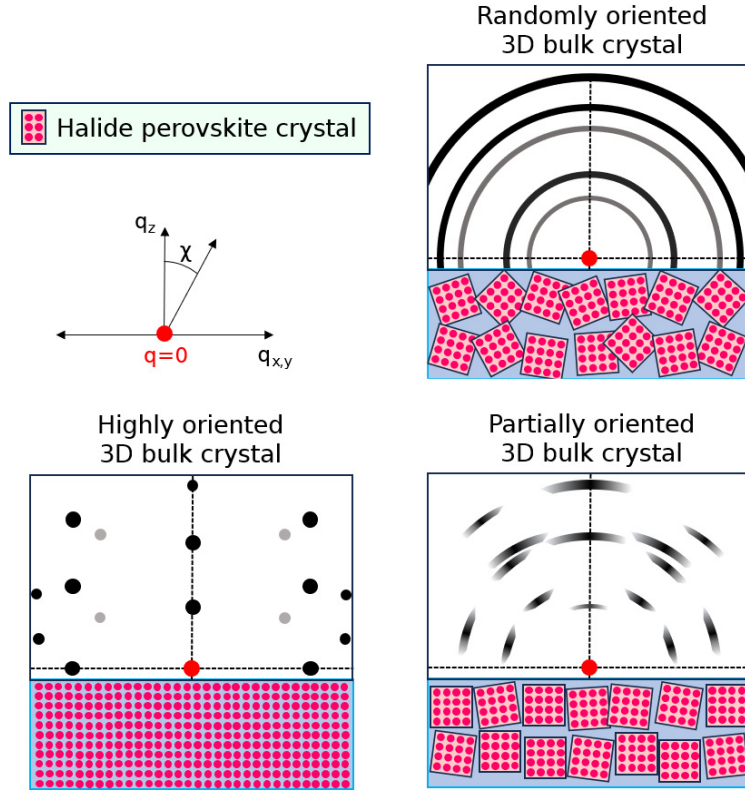


Figure 2.12.: Overview of common GIWAXS signatures for different oriented structural motifs and degrees of ordering in 3D perovskite thin films. Bragg peaks arising from the perovskite structure are depicted in pink, forming either points or rings, depending on their degree of orientation. Adapted from [8].

For 3D perovskites, typical X-ray scattering patterns are displayed in Fig. 2.12, including randomly, highly, and partially oriented perovskite crystallites. In general, the preferred orientation depends on the perovskite composition as well as the fabrication method. The scattering signals from 2D perovskite-like structures with dimensionality of $\tilde{n} = 1$ and $\tilde{n} > 1$ are presented in Fig. 2.13. For compositions with dimensionality $\tilde{n} > 1$, it is possible to observe a combination of 2D phases with different preferred orientations within one grown film [75, 76]. The preferred orientation of the perovskite phase can be extracted from the GIWAXS scattering data by plotting the scattering intensity profile depending on the azimuthal angle, calculated as $\chi = \arctan\left(\frac{q_x}{q_z}\right)$.

The crystallization processes include multiple steps: crystal nucleation and growth, and the formation/transformation of crystalline and non-crystalline intermediate phases [77]. Tracking an entire crystallization process from the precursor solution to the final film would benefit the research, as the precise characterization and the mechanistic pathways from the crystals to the perovskite phase are enabled by the *in situ* characterization facilities. The present work is driven by the necessity of controlling thin film fabrication mechanisms, and revealing the structural diversity of the formed phases.

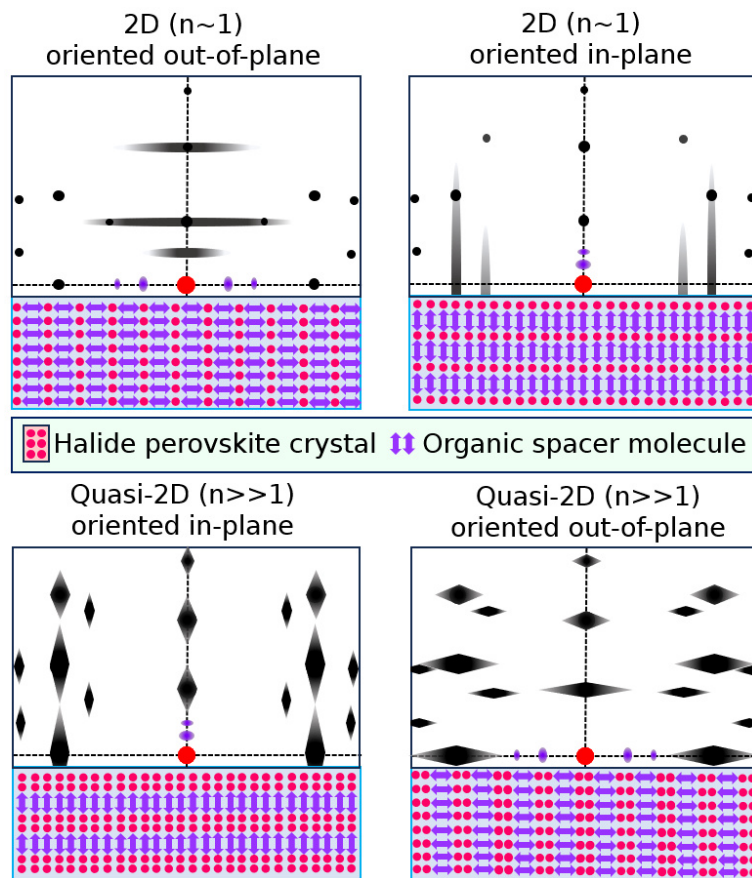


Figure 2.13.: Overview of common GIWAXS signatures for different oriented structural motifs and degrees of order in 2D perovskite thin films. Bragg peaks resulting from the perovskite structure are shown in pink. Diffuse scattering takes place in low dimensional system due to stacking defects, in addition to Bragg peaks. Quasi 2D systems and mixed $\tilde{n}$ - phase materials give elongated peaks orthogonal to the stacking disorder. Low dimensional 2D materials, $\tilde{n} \approx 1$, and systems which may also have 2D stacking defects, can give rise to relatively long streaks. Adapted from [8].

2.3. Solution-based thin film deposition

The following section describes a full cycle of thin film deposition from a precursor solution. It starts with the description of the substrate preparation, which involves ultrasonic bath cleaning, followed by plasma cleaning for substrate surface activation. Spin-coating is one of the most common techniques for thin film deposition. The one-step method features the deposition of all compounds dissolved in the appropriate solvent by spin-coating, followed by annealing. In order to improve thin film quality, antisolvent deposition or nitrogen stream assistance can be applied during spin-coating, both of these additional techniques are described below.

2.3.1. Substrate preparation

Before depositing the thin film, every substrate goes through a preparation sequence that involves ultrasonic bath cleaning and plasma cleaning. Ultrasonic cleaning is a fluid cleaning method that employs solvent cavitation as the driving force [78]. This approach is used to remove large contaminants and should not be relied upon as a final cleaning method. The selection of an organic solvent typically hinges on its proficiency in dissolving pollutants while creating minimal internal bubble pressure. Despite this, organic solvents offer better cleaning than water. In this study, $10 \times 10 \text{ mm}^2$ glass substrates with or without ITO coating (with thickness of $\sim 100 \mu\text{m}$) were treated with two organic solvents, namely isopropanol (IPA) and acetone, for 5 minutes each. The glass surface was treated with an argon plasma, resulting in physical cleaning of the glass surface after chemical cleaning. This process induced micro-etching, thus increasing the substrate surface and relatively improving surface hydrophilicity [79]. Furthermore, argon plasma cleaning is effective in preventing oxidation, a crucial factor for the materials studied in this work. Prior to thin film deposition in this study, all glass substrates underwent high-power argon plasma cleaning for 60 seconds (Fig. 2.14). Prolonged plasma treatment can etch the ITO layer, so a shorter treatment is recommended. The short treatment improved the wettability of the substrate and adjusted its surface functionality. This in turn resulted in improved coverage and thicker films with greater scattering intensity from the deposited thin films compared to the films on untreated substrates. The resulting decontaminated substrates were subsequently placed in the sample boxes.

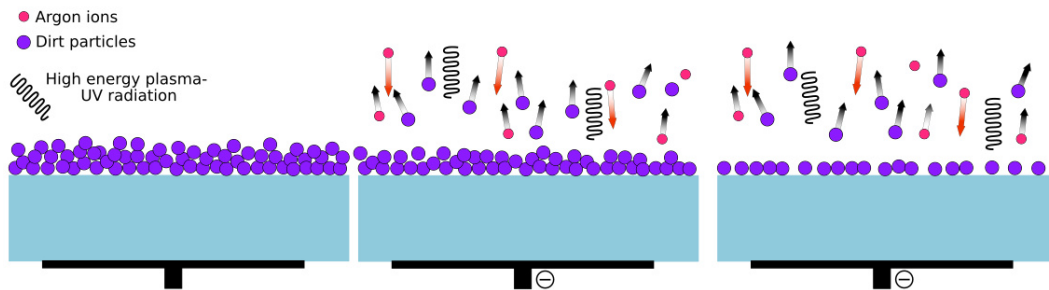


Figure 2.14.: Schematic illustration of argon plasma cleaning: physical etching mechanism by argon ion bombardment of the substrate surface. The kinetic energy of the argon ions (pink) causes ions, molecules and atoms (violet) to be removed from the surface.

2.3.2. Spin-coating

Organic and hybrid thin films are widely adapted for modern electronics and optoelectronics [80, 81]. In-depth analysis of their structural and optical properties enhances our comprehension of the thin film growth mechanism during preparation [82–84]. Spin-coating is especially crucial for creating samples on a laboratory scale. It is a fast and

straightforward technique that yields an ideal morphology for thin films with thickness ranging from a few nanometers to a few micrometers [20].

There are four distinct stages to the spin-coating process [85]. These include:

Deposition stage

The initial stage of a conventional spin-coating process involves the deposition of the precursor solution, as exhibited in Fig. 2.15(a). There are two widely used techniques for the dispense phase: *static* dispense and *dynamic* dispense. The static dispense is executed by locating a small amount of liquid ($\sim 40\text{--}60\ \mu\text{L}$ for a $10\times 10\ \text{mm}^2$ substrate) onto or in proximity to the center of the substrate [85]. The amount of liquid utilized is determined by both the solvent viscosity and the coating requirements of the substrate. For fluids with higher/lower viscosity or larger substrates, a larger amount of liquid is necessary, which can only be achieved through dynamic dispensing. The precursor solution is delivered while the substrate rotates at a relatively low speed, typically around 500 rpm [86]. This provides a necessary solution in cases where the substrate has poor wettability, thus preventing void formation [87] and improving thin film morphology [88].

Spin Up stage

This stage is characterized by the effective removal of the solution from the wafer surface by rotational motion, commonly referred to as the substrate acceleration stage [89]. The process is illustrated in Fig. 2.15(b), showing that a brief formation of spiral vortices is induced by the initial depth of fluid on the substrate surface. They form due to the twisting motion caused by the inertia of the top layer of fluid while the substrate beneath accelerates; i.e. $d\omega/dt \neq 0$. Gradually, the fluid becomes thin enough to fully co-rotate with the wafer, and any indications of differences in fluid thickness vanish. To optimize the spin-coating procedure, a combination of spinning speeds and times must be carefully selected, taking into account the various variables that tend to average and cancel out during the spin process.

Spin Off stage

At this stage the substrate is spinning at the constant speed and fluid viscous forces dominate fluid thinning behavior, as it is displayed in Fig. 2.15(c). The stable fluid outflow from the deposited film results in the gradual fluid thinning. Even though the fluid thinning is rather uniform, for the solutions with volatile solvents it is possible to see interference colors "spinning off", with decreasing speed as the coating thickness is reduced [90]. Once the substrate reaches the target frequency, and the fluid layer thins out enough, the viscous shear drag accurately counteracts the rotational accelerations. The final film thickness is ultimately determined by the chosen spin speed and time at this stage [89]. For Newtonian fluids, mathematical treatments of the flow behavior show

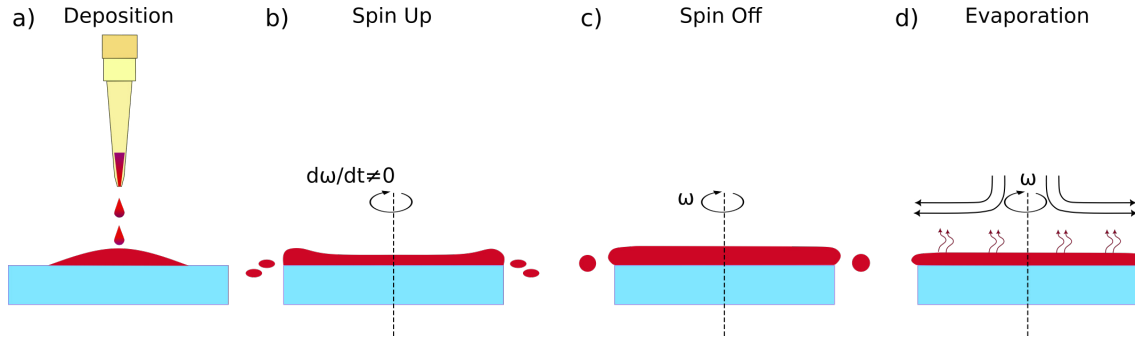


Figure 2.15.: Four distinct stages to spin-coating: (a) precursor solution deposition, which can be static or dynamic, depending on the liquid viscosity; (b) spin up stage, described as the removal of the solution due to rotational motion; (c) spin off stage, fluid viscous forces dominate thinning behavior; (d) evaporation stage, solvents evaporate due to their volatility. Usually evaporation stage during spin-coating is followed by the annealing treatment, which triggers the crystallization process.

that if the fluid thickness is initially uniform across the wafer (thick or thin), then the fluid thickness at any subsequent time will also be uniform [91]. Under ideal conditions, this will result in a uniform final coating [92].

Evaporation stage

As the third stage progresses, the fluid reaches a point where the centrifugal out flow stops. The subsequent stage leads to the volatilization of the solvents, which in turn becomes the primary mechanism for the decrease in thickness within the coating. The evaporation rate in this stage depends on the difference in partial pressure (chemical potential) of the each solvent species between the free surface of the liquid layer and the bulk of the nearby gas flow. If considerable evaporation takes place prematurely, a solid layer appears on the liquid surface which hinders the evaporation of solvent caught underneath it. This can have a significant effect on the crystallization process in the coated thin film. It is therefore essential to ensure accurate growth conditions. After spinning, it is often necessary to carry out heat treatment or "firing" of the coating in many applications, such as with "spin-on-glass" or sol-gel coatings [85].

A common spin-coating procedure is called one-step deposition, the details on this widely-used technique is discussed in Subsec. 2.3.3. A spin-coating procedure can be assisted by additional treatments, such as antisolvent application (Subsec. 2.3.4) or gas quenching (Subsec. 2.3.5), both methods are discussed in detail in next subsections. Their application and influence on the crystallization pathways of perovskite compositions are also presented in the current work.

2.3.3. One-step deposition

A common technique for producing thin films from the precursor solution is known as one-step deposition, named for the minimal number of steps required to produce a final film. The one-step fabrication technique is favoured for its ease of use, increased control over the manufacturing process, reduced number of parameters to monitor and higher device performance and reproducibility [93]. This procedure requires complete dissolution of all chemicals for the target composition using a solvent or solvent mixture. These solvents can be volatile or non-volatile [94], thus influencing the crystallization rate of the target structure. The most common solvents for organic-inorganic perovskite thin film fabrication are N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) [95]. In present work, the precursor solutions for the perovskite samples were prepared by dissolving the powder materials in pure DMF solvent or DMF/DMSO solvent mixture, the precise composition is announced in the beginning of each section. Mixing DMF and DMSO is balancing the high solubility of the precursor materials in DMF with the longer film drying times, caused by low volatility of the DMSO solvent [96–98].

A typical one-step method, used for thin fabrication in current work is displayed in Fig. 2.16. A clean substrate (cleaning is discussed in Subsec. 2.3.1) is fixed on a spinning rod by a vacuum chuck (commercially available spin-coaters), or on a sample table (custom built spin-coaters) by a vacuum chuck or by the heat-resistant sticky tape. The sample with deposited precursor solution is being spun at low speeds (typically 1000 rpm) for 10 s to distribute the precursor solution on the substrate surface, followed by spinning at a higher speed, for this work it was 4000 rpm, for 30 s. The second speed defines thin film thickness and can be reduced in the case of poor substrate coverage, since high efficiency of organic-inorganic solar cells can be achieved only with the uniform surface coverage without pinholes [99].

The one-step conversion method provides a straightforward and cost-effective approach to the fabrication of organic-inorganic thin films. This method involves growing solid-state perovskite thin films directly from a precursor mixture solution, which is induced by supersaturation [100]. A liquid film made of precursor solution on a substrates is displayed in Fig. 2.17. The solution deposition step, performed at ambient temperature, does not drive the complete conversion of the perovskite precursor materials [101]. In order to remove the solvent excess and cause supersaturation of the deposited thin films, several single methods or a combination of them can be used. The simplest and most widely used method to induce supersaturation is isothermal annealing [102]. Assuming that supersaturation of the precursor solution results in the appearance of perovskite species [103] (often referred to as "monomers", which can be molecules, atoms, ions, or formula units), they can cluster together into single crystal nuclei [100]. These nuclei are expected to emerge not only at the interface of the substrate/solution and colloidal particles/solution, but also within the precursor solution. The former and the latter are denoted as hetero-

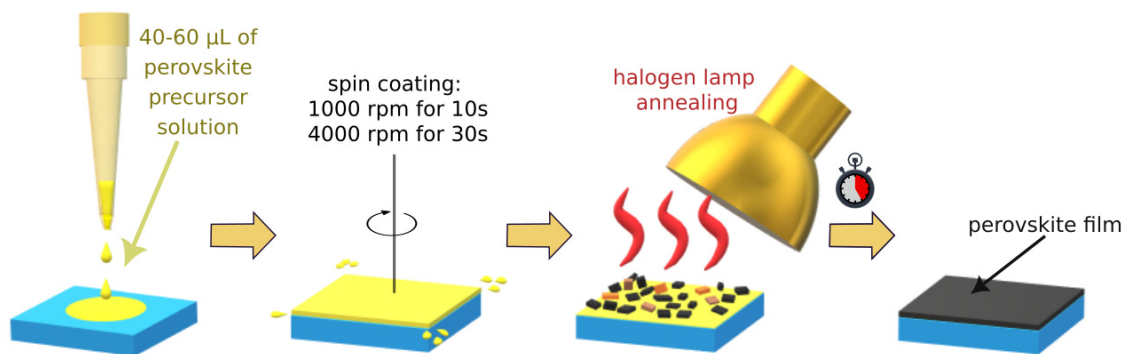


Figure 2.16.: One-step conversion method in the spin-coating chamber: 40–60 μL of the precursor solution is dropped onto a glass (bare or coated) substrate, spin-coated at 1000 rpm for 10 s, followed by spinning at a higher speed, typically 4000 rpm for 30 s. A halogen lamp is used to perform a subsequent heat treatment, resulting in thin film crystallization.

geneous and homogeneous nucleation, respectively. Different fabrication methods influence thin film nucleation by removing the solvent precursor: one-step method (marked as "evaporation"), antisolvent-assisted method (marked as "antisolvent application") and gas quenching (marked as "degassing"). The evaporation of the solvents naturally takes place during the one-step spin-coating procedure, as discussed in Subsec. 2.3.2.

The current subsection outlined a basic fabrication method using a direct spin-coating technique on the precursor solution without the need for additional treatment. Follow-up subsections will detail methods by which the fabrication process may be enhanced, through the introduction of supplementary steps during the spin-coating procedure. Antisolvent application during spin-coating [104–106] induces supersaturation of the deposited film, it will be discussed in Subsec. 2.3.4. Alternatively, gas-assisted preparation, also called gas quenching, can be supplied during spin-coating [107], it is presented in details in Subsec. 2.3.5. Both of them can be applied during thin film deposition and drastically change the energy distribution within the film. Their influence on thin film crystallization can be probed, for example, by *in situ* grazing incidence X-ray scattering techniques.

2.3.4. Antisolvent-assisted method

Present subsection is focused on general approach of antisolvent application during spin-coating of perovskite materials. The experimental procedure, which involves an antisolvent dripping, is displayed in Fig. 2.18. The solvent washing is an example of solvent engineering, which involves the deposition of a pure antisolvent [104, 108](toluene, chlorobenzene, isopropanol, ethanol, etc.) on the precursor film during casting (Fig. 2.17), thus inducing a rapid precipitation and partial crystallisation of precursor material over a few seconds. The solvent washing is clearly beneficial for the device performance, since relative efficiency

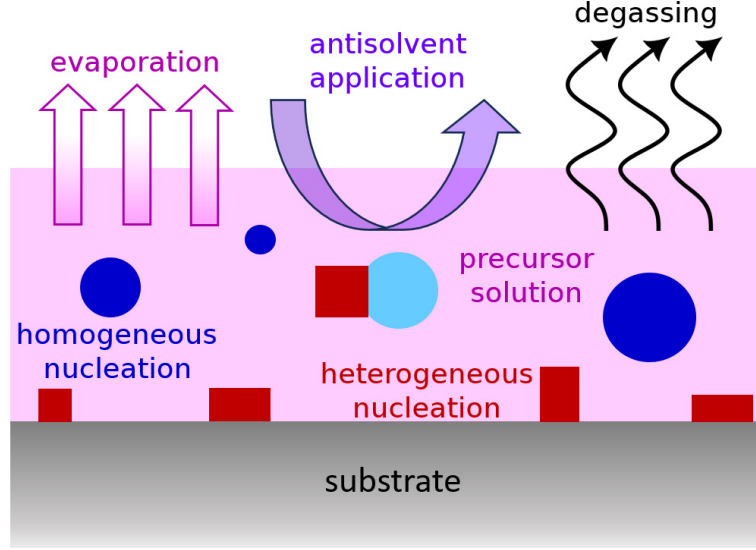


Figure 2.17.: Schematic illustration of the processes taking place within the deposited thin film. Evaporation takes place during spin-coating, while antisolvent or N_2 gas flow induce a faster supersaturation by removing the solvents. Classical nucleation is divided into heterogeneous, when nuclei are forming at the substrate/solution and colloidal particle/solution interfaces, and homogeneous, when nuclei emerge within the precursor solution. Adapted from [100].

improvements of up to 30% have been realized, its short duration may be frustrating for *in situ* characterization with X-rays [101]. At least two variables in the fabrication parameters for antisolvent-assisted method affect perovskite crystallization and final solar cell performance: antisolvent dripping time [109] and dripping rate [110]. There are many other hidden variables, which can affect the resulting thin film, such as light soaking, atmosphere before, during or after processing, temperature, and more other conditions, which are unique to each lab group and may affect the resulting film [111]. One of the strategies to widen an antisolvent dripping window is introducing an additive to slow down the crystallization process [112, 113]. Typically, chlorobenzene antisolvent application results in an immediate solution supersaturation [114]. The crystallization is then causes immediate homogeneous crystallization with very short incubation period.

Antisolvent application greatly affects the formation of different phases during thin film crystallization. The synthesis of $MAPbI_3$ perovskite using various antisolvents [115] has been demonstrated to generate the intermediate DMSO-based phase, whereas the introduction of the FA^+ cation into the mixture prompts the emergence of the 2H hexagonal phase. Subsequent modification of the composition *via* the addition of Br^- halides leads to growth along the 2H-4H-6H-perovskite pathway [71, 116]. The precursor solution, containing DMSO solvent, is more likely to gather at the edge of the substrate due to the strong coordination between the substrate edge and the DMSO-based precursor solution. The "green" antisolvent method can be done by selecting IPA, it induces the cleaning of the residual DMSO solvent, since IPA has a suitable boiling point and low viscosity [117].

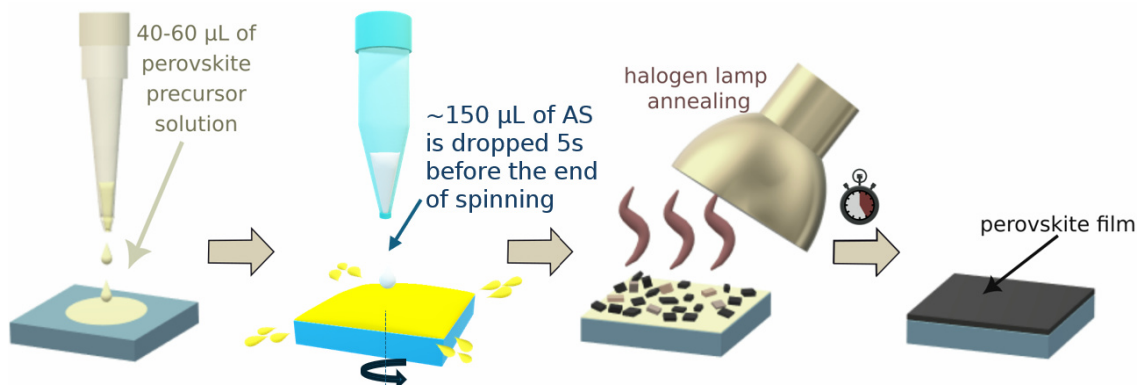


Figure 2.18.: An antisolvent assisted technique, the different step in comparison to one-step method is highlighted: 40–60 μL of precursor solution is dropped onto a bare or coated glass substrate, which is then spin-coated at an initial speed of 1000 rpm for 10 seconds, after which the rotation speed is increased to 4000 rpm for 30 seconds. Approximately 150 μL of antisolvent is introduced 5 seconds before the spinning process is completed. Subsequently, a halogen lamp is used to facilitate the heat treatment, inducing thin film crystallization.

Besides that, using a "green" IPA antisolvent in combination with fine composition tuning leads to a high-performing device with a PCE of 21.5% [118]. Present work includes a research on the effects of using IPA as an antisolvent on single- and mixed-cation compositions.

Present subsection introduced some features of the antisolvent-assisted spin-coating technique and highlighted the challenges of its application.

2.3.5. Gas quenching method

This subsection is focused on general approach of gas quenching treatment during spin-coating of perovskite materials. The use of a nitrogen flow during spin-coating speeds up the solvent evaporation process, as demonstrated in Fig. 2.19. The continuous gas flow is utilised to remove non-complexed solvent, resulting in the creation of the supersaturated intermediate state. This results in rapid saturation and smooth precipitation. Films with tightly packed grains can be quickly achieved through annealing [119]. This is a very promising and potentially more robust alternative to the antisolvent application, since the influence of solvent-solvent interactions in the liquid precursor phase is avoided [120].

The structural information of thin films can be probed by non-invasive X-ray scattering techniques, however it is necessary to design a special sample environment with a stable sample height during spinning as well as remote control of all the systems involved in the deposition procedure [1, 22, 23, 121]. Implementing *in situ* GIWAXS exposed the mechanism of film formation in the presence of nitrogen jet flow [114]. The gas stream effectively removed volatile liquids such as DMF and DMSO from the air-liquid interface (Fig. 2.17).

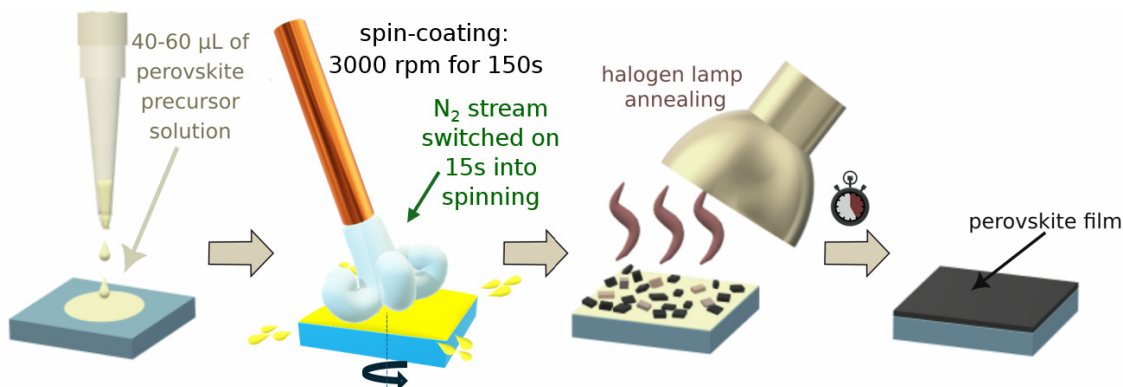


Figure 2.19.: Gas quenching-assisted method in the spin-coating chamber, the different step in comparison to one-step method is highlighted: 40–60 μL of the precursor solution is dropped onto a glass (bare or coated) substrate, spin-coated at 3000 rpm for 150 s, nitrogen stream switched on 15 s into spinning. A halogen lamp is used to perform a subsequent heat treatment, resulting in thin film crystallization.

Depending on the time, when nitrogen jet is applied, the incubation period, when crystallization starts, can be either long ($\approx 8\text{ s}$, earlier gas application) or short ($\approx 3\text{ s}$, later gas application). This originates from the reduced presence of volatile substances in the wet film. Upon reaching supersaturation, crystallization is believed to begin at the top interface of the wet film, with subsequent solidification occurring in both the bulk and the liquid-air interface [114]. The crystallization under nitrogen gas quenching treatment can be described as two stages. The first stage is initially characterized by vapor-interface-induced crystallization, which creates highly oriented crystallites. In the second stage, crystallization occurs through both nucleation and growth of crystals from the bulk, resulting in randomly oriented crystals in addition to the highly oriented crystals. The gas quenching method guarantees a decent performance of the devices, and demonstrates its feasibility of film deposition in ambient air. This feature makes it compatible with the upscalable techniques, such as slot die or doctor blading [122].

2.4. Combination of in situ X-ray scattering and spin-coating

The current chapter introduced the fundamentals of X-ray scattering and solution-based deposition technique, spin-coating. The main goal of this work was to combine *in situ* characterization and thin film fabrication process, which resulted in designing a spin-coating chamber with embedded devices. The resulting infrastructure item in general can be used for depositing various solution-based compositions, and the crystallization kinetics between the precursor solution deposition and the target phase can be resolved.

3. Perovskite structure

Present chapter is dedicated to the materials, studied in current work, namely hybrid perovskites. Hybrid lead-based organic-inorganic perovskite solar cell materials, first discovered in 2009 [123], are extensively researched due to their high efficiencies and low production cost. They have either conventional three-dimensional structure, or 2D/quasi-2D structure with a large hydrophobic spacer cation, improving their stability. Both of these structures, as well as solvent-based and solid intermediate phases, found in the studied compositions, are described in details. In the end, features of GIWAXS characterization on perovskites is shown.

3.1. 3D perovskites

Perovskite is a crystal structure with a chemical formula ABX_3 , as displayed in Fig. 3.1 with examples of particular molecules and atoms studied in current work. The high bandgap tunability of perovskite solar cells can be achieved by choosing an appropriate composition, which includes a design based on ionic radii of the cations and halides, mixed for the desired composition. The stability of perovskite compositions can be affected by various factors, the transition of intermediate non-perovskite phase to perovskite phase occurs at specific temperatures depending on the mixing ratios of cations and halides within the composition. In general, materials with ABX_3 composition are able to adapt different crystal structures besides target perovskite structure. It is based on the ionic radius of the A-cation and its interaction with the corner-sharing BX_6 octahedra. An empirical index for prediction of preferentially formed structure is called Goldschmidt tolerance factor (t) [124]. It is calculated from the ionic radius of the atoms within the composition using the following expression:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (3.1)$$

where r_A and r_B are ionic radii of the A cation and B cation, respectively, while r_X is the radius of the anion. The organic-inorganic halide perovskite materials exhibit an orthorhombic structure when $t < 0.8$, cubic structure when $0.8 < t < 1$, while for $t > 1$ hexagonal structure is being formed, as it is shown in Fig. 3.2(a). Usually more than one crystal structure is found for each composition, it often depends on the fabrication method and the growth temperature. The current work is focused on studying perovskites

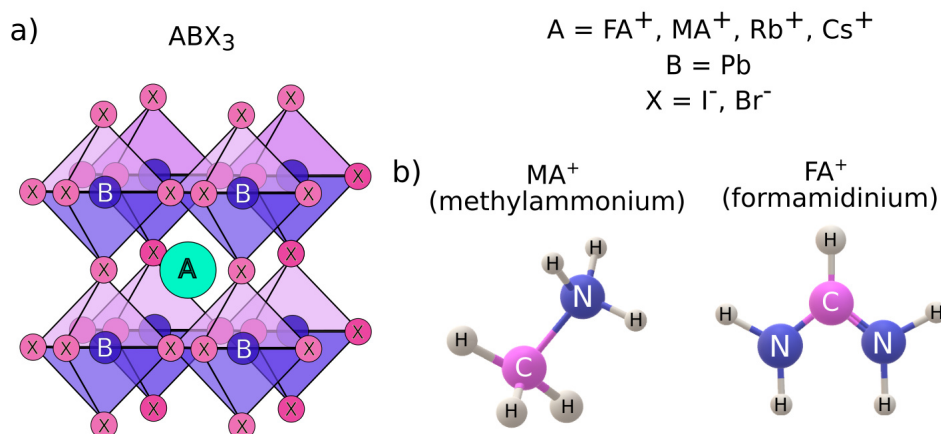


Figure 3.1.: (a) Perovskite cubic crystal structure with formula ABX_3 , where $A = MA^+$, FA^+ , Rb^+ , Cs^+ , $B = Pb$ and $X = I^-$ or Br^- ; (b) two most applicable organic cations methyammonium (MA) and formamidinium (FA).

including MA^+ , FA^+ , Cs^+Rb^+ or their mixtures for A site cation, Pb as B site cation and I^- or Br^- or their mixtures as X anion. A desired perovskite phase is typically referred to as α -phase, while the undesired phases, such as hexagonal or orthorhombic, are referred to as δ -phases.

Most common perovskite composition, methyammonium lead iodide ($MAPbI_3$), lacks environmental stability[125] and tends to convert into tetragonal phase at $T \approx 55^\circ C$ [126]. As a potential alternative, formamidinium (FA) is widely investigated [127], however, formamidinium lead iodide ($FAPbI_3$) lacks structural stability at room temperature and tends to convert from the photoactive cubic α -phase (black) to hexagonal δ -phase (yellow) [128]. The difference in phase behaviour of MA and FA can be accounted for by the different sizes and hydrogen bonding mechanisms of these dissimilar organic cations [129]. There are various strategies to overcome environmental and structural instability [130], including solvent engineering [113, 131–133] and mixing multiple cations and halides [134–137]. Lacking stability of single-cation perovskites under ambient conditions has led to compositional and solvent engineering, involving addition of inorganic cations, such as Cs^+ and Rb^+ , which stabilize the perovskite phase [138–142]. The simple deposition of a precursor solution containing all the reactants is defined as "one-step process", while the additional treatment during spin-coating such as antisolvent application [72, 115, 116] or gas quenching [15, 119, 143] often improves perovskite film quality and accelerates the crystallization by removing the solvents.

3.2. Intermediate phases

Present subsection describes intermediate phases which are observed within the studied perovskite compositions, including solvent-based and solid state intermediate phases. Both

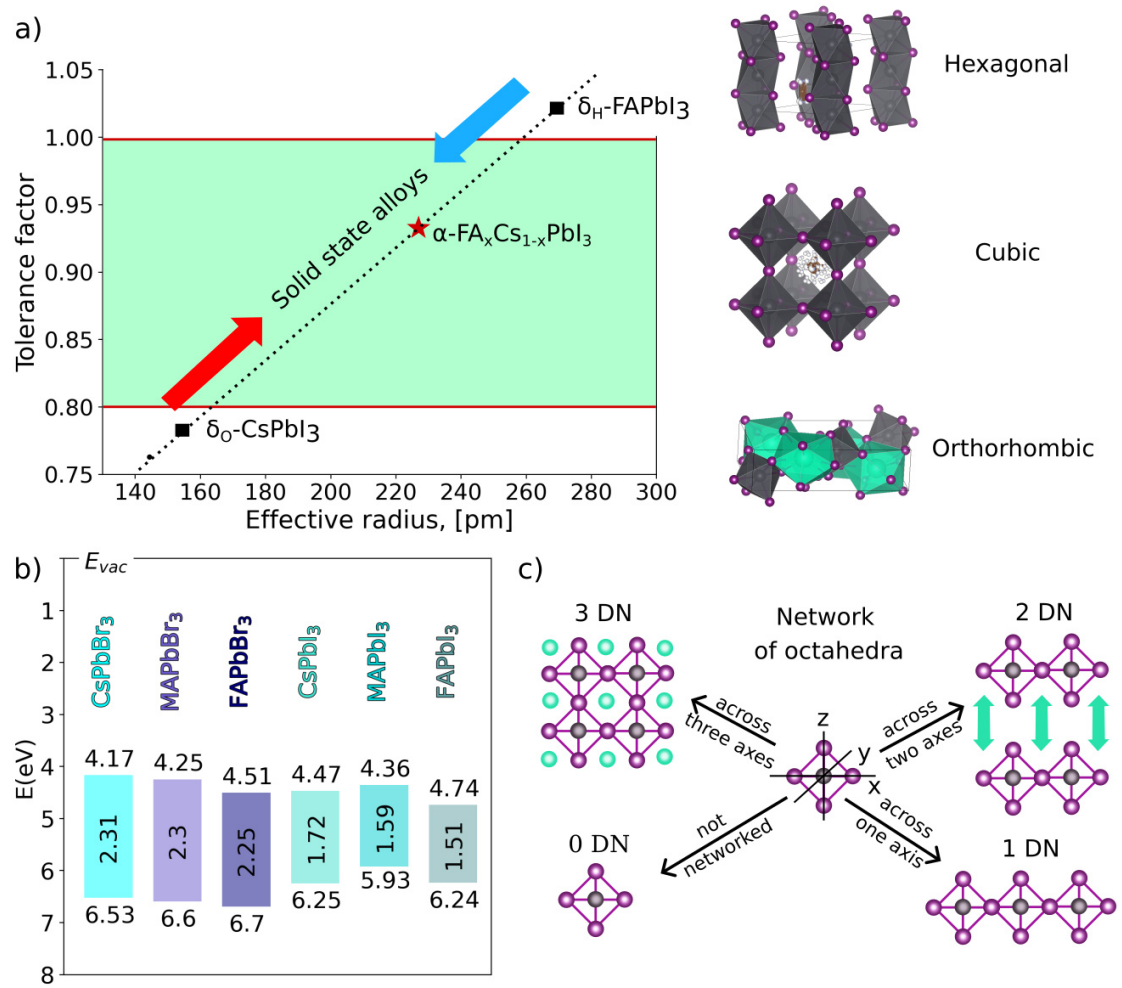


Figure 3.2.: (a) Correlations between tolerance factor and crystal structure of perovskite materials [144]; (b) Schematic energy level diagram of the 6 metal halide perovskites, studied and mixed in the current paper. The respective ionizing energy and electron affinity values as well as the optical gaps (all in eV) are sorted in order of decreasing band gap. The optical gap was extracted from the UV-Vis measurements [145]; (c) Dimensionality of perovskites based on the networks of octahedra [146].

types can appear in the deposited thin film as a preliminary step before perovskite phase formation, and can be converted into the target structure upon annealing.

3.2.1. Solvent-based intermediate phases

Present paragraph displays solvent-based intermediate phases based on DMF and DMSO, two common non-volatile solvents used for preparation of all the compositions, discussed in current work. For the DMF solvent, the phases with one, two and four intercalated molecules were observed. The DMF-based structures are displayed in Fig. 3.4, namely (FA)₂Pb₃I₈·4DMF [147], FAPbI₃·2DMF [147] and MAPbI₃·DMF [98]. One more struc-

ture was potentially detected during FAPbI₃ composition growth, which presumably has a chemical formula of FAPbI₃·DMF [148]. Previously it was artificially obtained by toluene washing and vacuum drying, while in current work it was observed during the crystallization of FAPbI₃ composition dissolved in DMF, deposited by different methods. such as one-step conversion, ethanol antisolvent application and gas quenching. In general, DMF solvent by nature is not volatile, but it is more volatile than DMSO [94], which is also frequently used as a precursor solvent. In current work we demonstrate that FA is able to form intermediate phases with DMF, which then sequentially transform into the 2H hexagonal phase and turn into perovskite phase upon annealing. The detailed evolution of both FA- and DMF-based intermediate phases is shown in Subsec. 5.4.1.

A typical DMSO-based intermediate phase, which forms in pure MAI-based per-

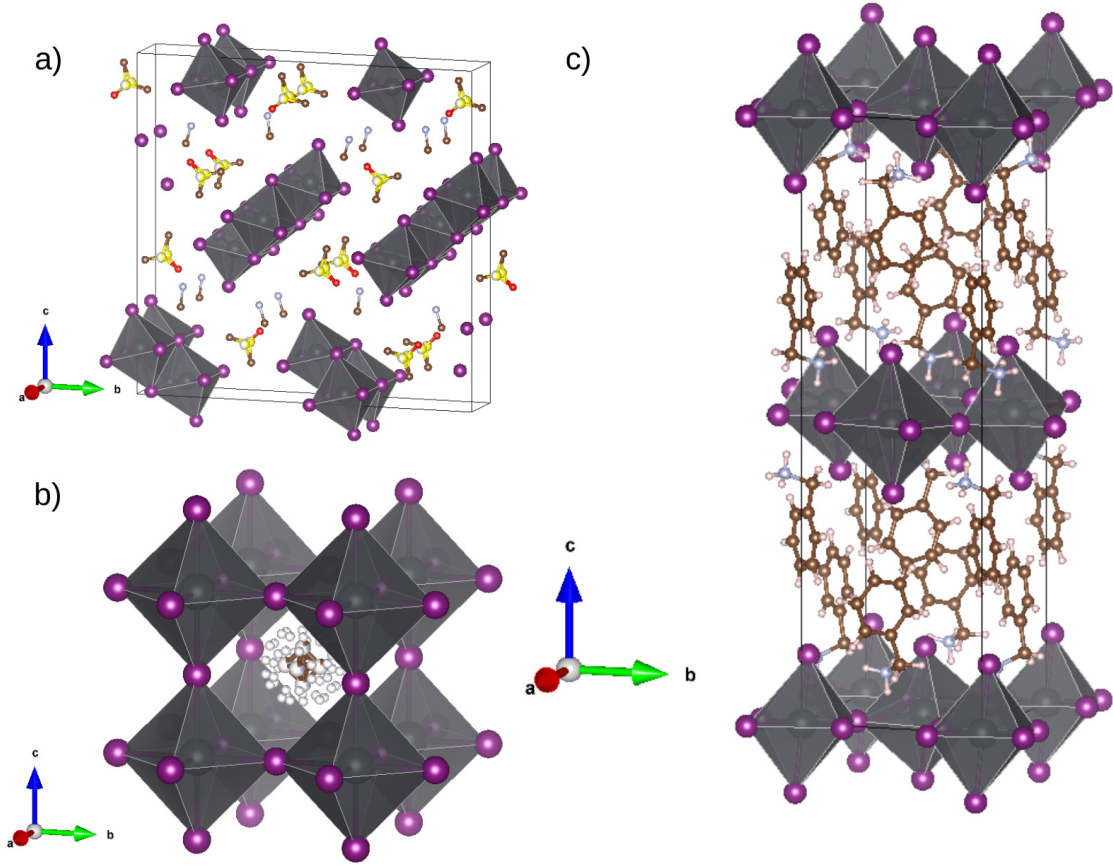


Figure 3.3.: Crystallographic view of perovskite-related structures: (a) solvent-based intermediate phase MA₂Pb₃I₈·2DMSO [131]; (b) MAPbI₃ 3D perovskite phase [149]; (c) (BNA)₂PbI₄ 2D Ruddlesden-Popper $\tilde{n} = 1$ layered perovskite phase [150]

ovskites and mixed cation perovskites with 1:1 and 4:1 DMF:DMSO solvent mixtures, is (MA)₂Pb₃I₈·2DMSO [151, 152]. Its crystal structure is displayed in Fig. 3.3(a), it can be described as triple-chains of edge-sharing PbI₆ octahedra with all unshared apexes sitting

at their sides. In general, this phase starts its transformation at elevated temperatures, around 73°C as it was obtained by thermogravimetric analysis of this phase in a form of a single crystal [151]. On the other hand, smaller crystallites within a thin film show the conversion into perovskite phase at 55°C. For mixed cation compositions this structure is observed as a dominant MA-based structure, which upon annealing mixed with other A-site cations (such as FA⁺ and Cs⁺) and/or halides and created mixed perovskite phase [116], which then has a tetragonal structure due to the presence of MA⁺ cations within the phase.

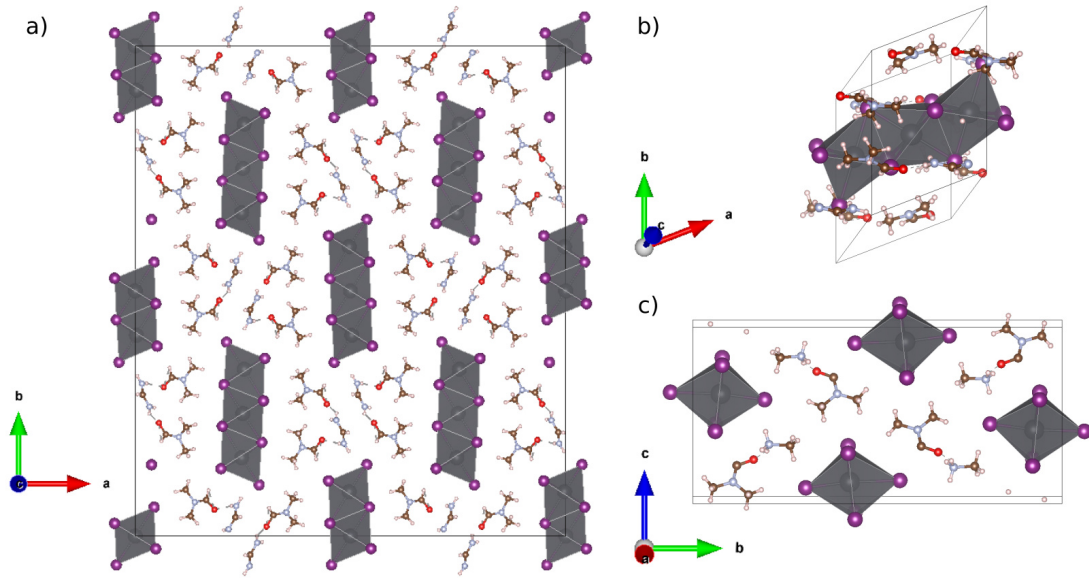


Figure 3.4.: Crystallographic view of perovskite-related structures: (a) (FA)₂Pb₃I₈·4DMF [147]; (b) FAPbI₃·2DMF [147]; (c) MAPbI₃·DMF [98]

3.2.2. Solid state intermediate phases

Present paragraph shows typical solid state intermediate phases of perovskite-based compositions. These include hexagonal and orthorhombic phases. A pure FAPbI₃ composition adopts 2H hexagonal structure at room temperature, as it is displayed in Fig. 3.2(a) and denoted as δ_H -FAPbI₃ [153]. In order to improve the perovskite phase stability and solar cell power conversion efficiency, mixing cations and halides is widely implemented [71, 134, 154]. There are several additional hexagonal phases, existing for FA-dominating mixed-cation and mixed halide perovskite compositions, such as 4H and 6H polytypes. Their crystal structure as well as stacking sequence are displayed in Fig. 3.5. As one can follow the trend, the face sharing of the PbI₆ octahedra leads to a 1D array (2H), while corner-sharing favors a 3D framework, resulting in perovskite phase. A linear combination of corner- and face-sharing octahedra results in formation of higher order polytypes, such as

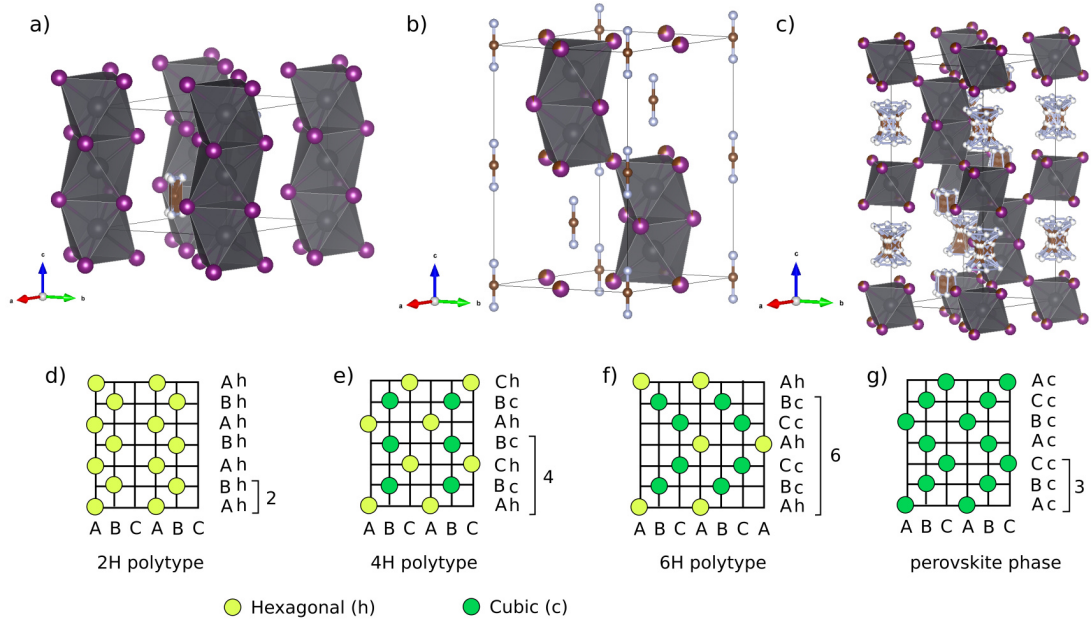


Figure 3.5.: Crystallographic view of hexagonal phases: (a) 2H hexagonal polytype; (b) 4H hexagonal polytype; (c) 6H hexagonal polytype. Comparison of the AX_3 stacking sequence (h: hexagonal close-packed, yellow circles; c: cubic close-packed; green circles) between three different hexagonal lead halide polytypes: (d) 2H polytype, (e) 4H polytype, (f) 6H polytype and (g) perovskite phase. Illustration is adapted from [71].

4H and 6H, which are typically observed as intermediate states between the 1D 2H hexagonal phase and a desired perovskite phase in mixed cation and mixed halide compositions, such as $FA_{0.83}MA_{0.17}Pb(I_{0.83}Br_{0.17})_3$ (denoted as FA:MA) [71, 116]. For example, the crystallization sequence of the FA:MA composition induced by chlorobenzene antisolvent application was found to be:



Soon after the antisolvent application, 2H and 4H dominated the crystallization, and then rapidly converted into the 6H phase. In order to complete conversion to perovskite, the annealing procedure was required. This transition pathway coincides with the density functional theory (DFT) calculations for the $FAPbI_3$ and $FAPbBr_3$ compositions: the formation energy (ΔH) for both of the compositions is the highest for the 3D cubic perovskite phase [30]. The incorporation of Cs^+ inorganic cation into the FA:MA composition suppresses the formation of thermally stable 4H and 6H phases, which results in the direct formation of perovskite phase prior to annealing, since its relatively small ionic size pushes the tolerance factor toward the appropriate α -phase range (Fig. 3.2). This was also predicted by the DFT calculations, since the Cs^+ cations can lower the formation energy

of the target perovskite phase [30]. The perovskite properties are essentially being tuned by the multication compositions, featuring cations with different ionic radii, which then occupy different positions within the perovskite phase. The A-site alloying improves both stability and reproducibility of the perovskite solar cells. The role of different A-cations in the growth process and their distribution in mixed A-cation perovskite lattice and the structural heterogeneity are still to be explored [155].

Another intermediate phase, observed for perovskite compositions ABX_3 , is an orthorhombic phase, which δ_O -CsPbI₃ composition adapts at room temperature, it is displayed in Fig. 3.6(a). The tolerance factor of an orthorhombic crystal phase is below 0.8 as it is marked in Fig. 3.2(a). According to the literature [156], the conversion into cubic perovskite phase takes place at $\sim 330^\circ\text{C}$. The addition of a small amount ($\sim 5\%$) of Cs⁺ as an inorganic cation into the mixed cation FA:MA perovskite composition reduces the trap density [157]. The addition of both Cs⁺ and Rb⁺ inorganic cations, 5% of each, into the FA:MA composition improves perovskite quality even further: it reduces the trap density and enhances the mobility of charge carriers, as it is displayed in Fig. 3.6(b). The crystallization pathways of such complex compositions are studied in Sec. 5.2.

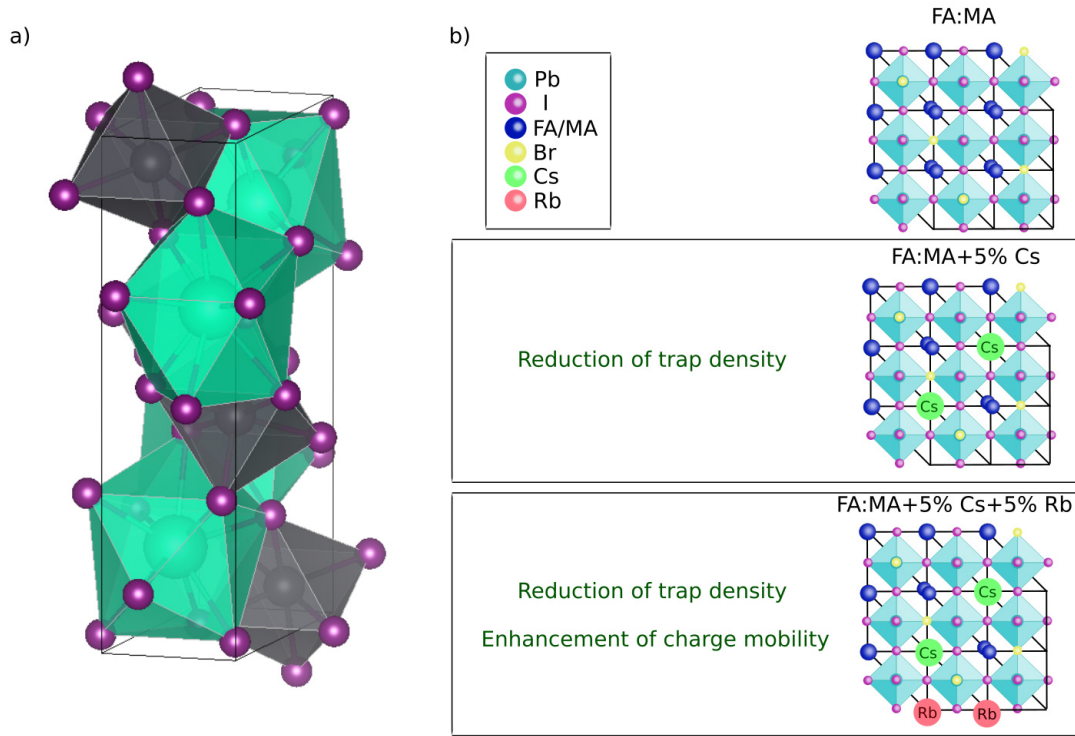


Figure 3.6.: (a) Crystallographic view of an orthorhombic CsPbI₃ phase. Structural information source: [156]. (b) Schematic illustration of the hypothesized distribution of the inorganic cation additives within the perovskite crystal and the effect of Cs/Rb addition to the FA_{0.83}MA_{0.17}Pb(I_{0.83}Br_{0.17})₃ (FA:MA) composition on the reduction of trap density and enhancement of charge carrier mobility within the perovskite layer, adapted from [157].

3.3. 2D perovskites

The crystal lattice of a 3D perovskite exhibits signs of damage under ultraviolet irradiation, at high temperatures and under ambient (moisture-rich) environments, which lead to the degradation and decomposition of the active light-sensitive material, resulting in device performance decrease [158, 159]. The relevant organic compositions with hygroscopic molecules display an intake of water into thin film which is detrimental for the long-term stability of perovskite phase. Low dimensional 2D perovskites have attracted considerable interest due to their long charge carrier lifetimes, high photoluminescence efficiency, and great defect tolerance [127, 160]. The presence of a larger organic cations between hybrid perovskite slabs results in the arrangement of layered perovskite architectures which leads to the enhanced stability under ambient conditions and suppressed internal ion migration [161]. Similar to 3D perovskites, 2D perovskite structures consist of organic and inorganic layers [162–164].

There are three connectivity modes in 2D perovskite structures: edge sharing, corner

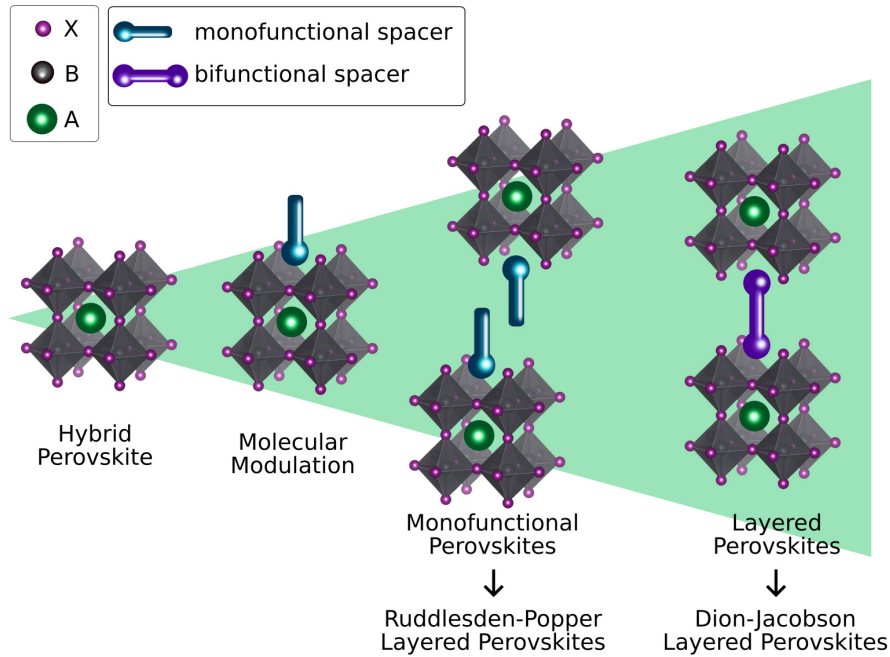


Figure 3.7.: Schematic representation of the evolution of hybrid perovskites: their molecular modulation and the formation of layered perovskite analogues, resulting in RP (monofunctional spacer) and DJ (bifunctional spacer) 2D phases. Adapted from [164].

sharing and face sharing [165]. The formation of only edge sharing and face sharing modes is rather rare due to the difficulties in the area filling of 2D perovskites [166]. Therefore, most of 2D perovskites exhibit the configuration with corner sharing octahedra. This type is further categorized by the lattice plane, along which 3D perovskite is sliced, includ-

ing: (100), (110) and (111) [165]. The layered hybrid perovskite materials are based on $S_xA_{n-1}B_nX_{3n+1}$ compositions which include organic (primarily ammonium-terminated) cations, which are either mono- ($x=2$) or bifunctional ($x=1$) and act as spacers (S within the formula) between hybrid perovskite layers (Fig. 3.7). The (100) structures are further divided in two groups, namely Ruddlesden-Popper [167] (RP) and Dion-Jacobson [168, 169] (DJ) phases, both of them are displayed in Fig. 3.7. The basic difference between these two phases is that the RP structure has two monovalent cations in the interlayer space, while the DJ structure possesses a single divalent (+2) spacer cation [166]. From the crystallography point of view, it is evident that RP perovskites exhibit a $(1/2,1/2)$ shift along the ab plane, while the DJ perovskites show $(1/2,0)$ shift or no shift along the ab plane (Fig. 3.7). A typical two dimensional (2D) perovskite structure with a target dimensionality of $\tilde{n} = 1$ is displayed in Fig. 3.3(c) and has a chemical formula of $(\text{BNA})_2\text{PbI}_4$, where BNA stands for benzylammonium ($\text{C}_7\text{H}_{10}\text{N}$). The broad structural diversity of 2D hybrid perovskites is greatly granted by the different layer thicknesses, so-called target dimensionality $\tilde{n}$. The 2D perovskite structures with $\tilde{n} = 1-3$ are displayed in Fig. 3.8(a-c).

It is important to highlight the differences between the orientations of 2D perovskite

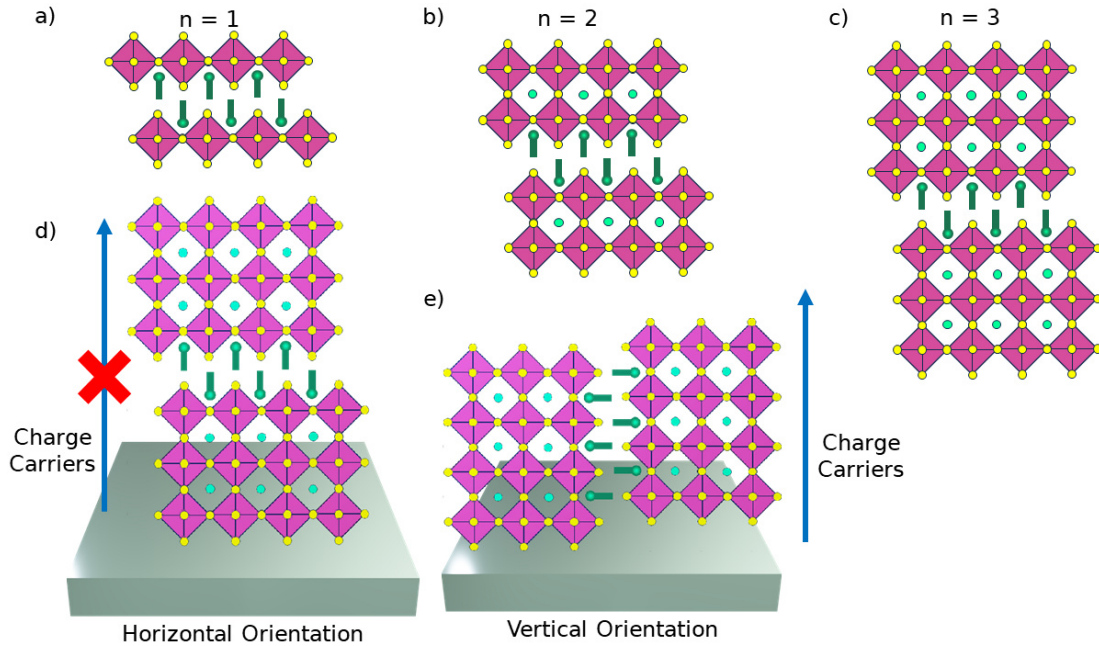


Figure 3.8.: Crystal structures of 2D perovskites with dimensionality (a) $\tilde{n} = 1$; (b) $\tilde{n} = 2$ and (c) $\tilde{n} = 3$. Schematic of charge carrier transport in 2D perovskites depending on its orientation relative to the substrate: (d) Horizontal orientation (in-plane) and (e) Vertical Orientation (out-of-plane). Illustration adapted from [44].

relatively to the substrate, as displayed in Fig. 3.8(d-e). In general, horizontal orientation (in-plane) of the 2D perovskite prevents charge carrier transport, however it can be used for the 3D perovskite phase stabilization. The vertical orientation (out-of-plane) ensures

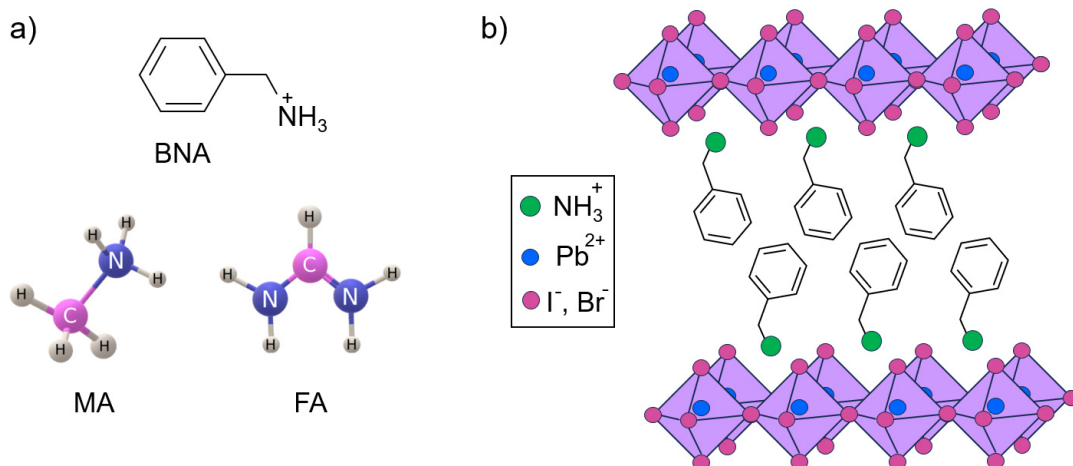


Figure 3.9.: (a) Molecular structures of BNA organic spacer cation and organic cations MA and FA for $\tilde{n} > 1$ compositions. (b) Illustration of layered RP perovskite structure based on $(\text{S})_2\text{PbX}_4$ composition.

reliable charge carrier transport and is beneficial for solar cell applications. There are various studies focused on producing 2D perovskite phases with the desired vertical orientation. In particular, the crystallization from liquid-solid interface results in a preferably vertical orientation of the forming 2D perovskite phase [170]. Note that in the results section the orientation of 2D perovskites is discussed relative to the spacer cation.

One of the frequently used molecules for layered perovskite structures is BNA, shown in Fig. 3.9(a). It has been reported to show slightly better photovoltaic performance than other common spacer cations, since it features high hole conductivity and simultaneously low energy onset for electron conductivity [171]. This molecule by the classification is a monofunctional organic spacer, the resulting 2D structures will be RP phase [164], as displayed in Fig. 3.9(b). The BNA spacer cation can be easily functionalized to tune material properties and increase the performance of optoelectronic devices, based on it [172]. Apart from photovoltaic applications, asymmetric functionalization opens possibilities for various other applications such as non-linear optics [150], piezoelectrics [173] and non-volatile memory switchers [174]. Even the parent BNA spacer cation has been shown to be applicable for different purposes, including layered materials for white light emission [175] and stabilizing the perovskite phase in 3D perovskite materials [176].

The complexity of perovskite thin film growth, already quite high and influenced by many factors for the commonly used 3D materials, is further increased when fabricating (quasi-)2D perovskite thin films. This is partly due to the possibility to form layered phases with different ratios of small and large cations, resulting in different thicknesses of the inorganic layers (designated by the number of lead halide layers n , as displayed in Fig. 3.8(a-c)) and their frequent coexistence [76]. Secondly, because of the anisotropic nature of the layered phases, the crystallite orientation is a relevant factor to consider

when preparing thin films intended for device usage. These aspects render the understanding of crystallization and thin film growth valuable knowledge to be able to tune the fabrication conditions for the desired results. However, except for growth investigations in solution [177], real-time studies of the growth of BNA-based layered perovskite thin films are rare.

2D perovskites, based on bifunctional spacer cations, and forming DJ phases, were

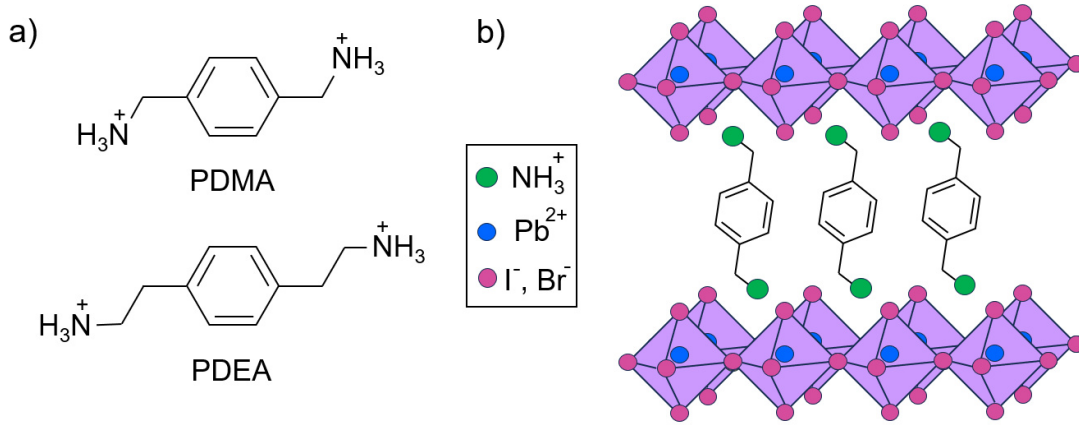


Figure 3.10.: (a) Molecular structures of PDMA and PDEA organic spacer cations. (b) Illustration of layered DJ perovskite structure based on (S)PbX₄ composition. Adapted from [178].

also studied in current work, to obtain the differences, caused by the spacer cation type. In particular, some compositions, based on phenylene-derived aromatic spacers, which were studied previously by *ex situ* GIWAXS [178], were investigated during their fabrication process. The chosen spacer cations are presented in Fig. 3.10(a), and are namely 1,4-phenylenedimethylammonium (PDMA) and 1,4-phenylenediethylammonium (PDEA). Both of these spacer cations showed their ability to form layered phases, while the size and orientation of the spacers was found to impact the charge transfer exciton formation [179]. Therefore, both compositions were studied with iodide and $n = 1$. As the length of the alkyl chain increases, the emission bandwidth and optical band gap also increase [178]. Additionally, since (PDMA)Pb(I_{0.5}Br_{0.5})₄ composition exhibits halide segregation upon light illumination [180], the PDMA- and bromide-based composition was investigated. The chosen spacer cations exhibit an increasing resistance to water with increasing alkyl chain length, while replacement of the iodide with bromide is also proven to be an effective strategy in improving its stability against moisture [178].

Part II.

Results and Discussion

4. Compact sample environment

The present chapter describes each system within the custom-built spin-coating environment for *in situ* X-ray scattering experiments and is partially based on a publication in the Review of Scientific Instruments [36]. This work was based on the SpincX infrastructure project funded by BMBF and tested at DESY. The final compact sample environment will be installed at the P08 beamline [181] at PETRA III, DESY.

Scientific experiments at synchrotron facilities bring strict requirements and limitations for the chambers designed, such as chamber size, weight, distance between the base plate and an X-ray beam, and remotely controlled devices. The latter requirement originates from the placement of the spin-coating chamber in the experimental hutch and its exposition to X-rays; this hutch cannot be accessed by synchrotron users during the experiment for safety reasons. Experiments at synchrotron facilities ultimately require remote control of the devices with their software being integrated into the local infrastructure (for example, *via* PyTANGO). This feature allows to control all devices from the main computer in the control hutch and automatically start spinning, antisolvent application, or gas quenching, and subsequently anneal the sample to follow the exact production procedure and get the resulting film. Since the grazing incidence geometry is characterized by a low angle of incidence of an X-ray beam, even a small deviation of it leads to the change in the probing depth, which is crucial for surface-sensitive *in situ* scattering experiments. The goal of the present work was to design and develop a compact sample environment for *in situ* grazing incident X-ray scattering measurements during spin-coating with its software implemented in the beamline infrastructure. Multiple chambers for thin film characterization during spin-coating based on X-ray scattering were developed previously [13, 182–184]. A brief overview of spin-coating systems, developed in the past, is shown in Tab. 4.1. The maximum frequency used for *in situ* spin-coating, was 4000 rpm. The spin-coating chamber, designed in the current work, has maximal frequencies of up to 10000 rpm. In combination with structural properties, studied by *in situ* GIWAXS, systems were designed to monitor optical properties: UV-Vis spectroscopy [183], polarized optical microscopy [24], optical reflectance [185] and differential reflectance spectroscopy (DRS) [36]. The atmosphere control system involves the presence of sensors (humidity and/or oxygen) that are necessary to monitor experimental conditions during perovskite thin film fabrication, it was realized for some experimental chambers [116]. Alongside with atmosphere monitoring, visual observation is essential to track changes in thin film color and texture [24]. Annealing is a typical post-processing treatment for spin-coated thin films and, due to the geometrical

Table 4.1.: List of spin coaters used for *in situ* WAXS measurements at different synchrotron facilities with key parameters: maximum frequency and implemented systems

Beamline and synchrotron	Maximum spinning frequency, [rpm]	Systems	Source
BL23A at NSRRC (Hsinchu, Taiwan)	1500	dispensing, spinning, UV-Vis spectroscopy, annealing	[183]
XRD2 at LNLS (São Paulo, Brazil)	4000	dispensing, spinning, atmosphere control	[116]
D1 at CHESS (NY, USA)	2000	spinning, polarized optical microscopy, surveillance	[24]
8-ID-E at Advanced Photon Source (IL, USA)	4000	dispensing, spinning, optical reflectance	[185]
I07 at Diamond Light Source (Rutherford, U.K.)	1500	dispensing, spinning	[23]
I07 at Diamond Light Source (Rutherford, U.K.)	1660	dispensing, spinning	[186]
BL03XU at SPring-8 (Hyogo, Japan)	3500	dispensing, spinning	[13, 22]
12.3.2 at Advanced Light Source (CA, USA)	6000	dispensing, spinning, photoluminescence, surveillance, annealing, IR camera	[187]
P08 at DESY (Hamburg, Germany)	10000	dispensing, spinning, gasquenching, atmosphere control, DRS, surveillance, annealing	this work

complexities of the chamber, this process is carried out using an infrared heater that is directed at the surface of the thin film [183].

Our setup meets the challenge of minimum wobble at high rotation speeds, which is crucial for GIWAXS, and also has complementary sample manipulation and characterization tools. In this chapter a detailed description of the remotely operated systems is presented. The designed chamber is dedicated for GIWAXS measurements at beamline P08 [181] at PETRA III/DESY and fits on any beamline with a hexapod. We tested the performance of our compact sample environment by studying the crystallization pathways of different perovskite compositions during spin-coating and annealing in real time by *in situ* GIWAXS.

4.1. General concept

The general concept of the sample environment is shown in Fig. 4.1(a). The main part of the experimental setup consists of a cuboid housing (225 mm (vertical) $\times$ 210 mm $\times$

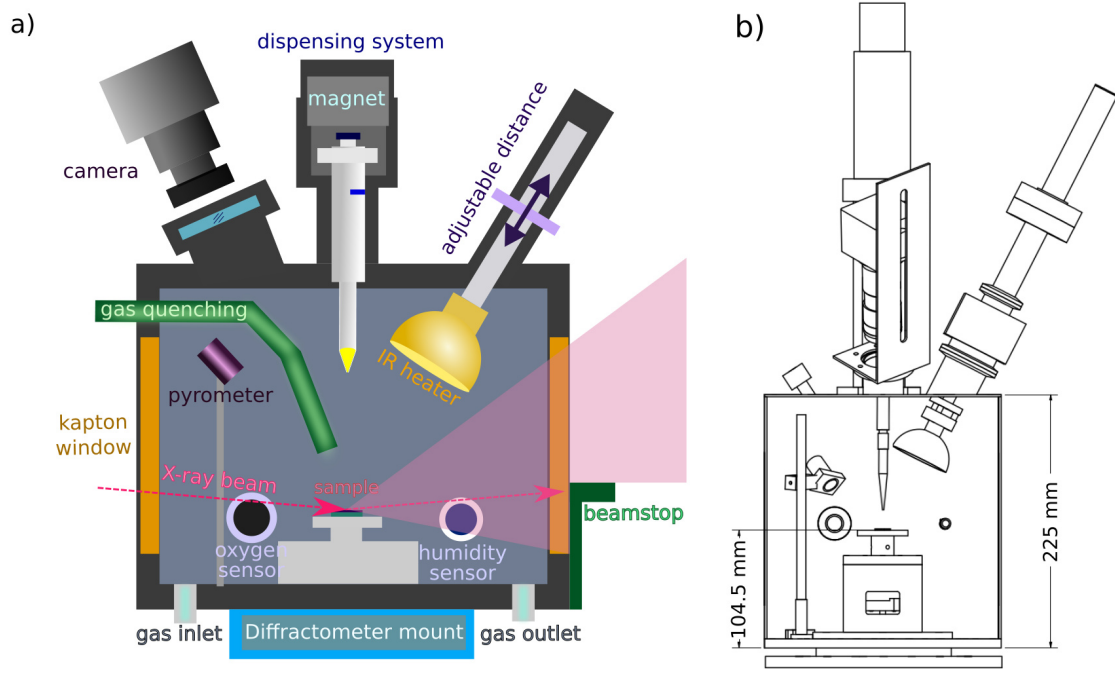


Figure 4.1.: Spin-coating chamber for *in situ* GIWAXS measurements: (a) general concept including all the major parts; (b) technical drawing of the chamber imported from Autodesk Inventor 2020 Certified Professional.

210 mm) made of stainless steel with kapton windows for incident and scattered X-rays. The size of the window for the scattered X-rays is 120 mm (horizontal) $\times$ 90 mm (vertical) to cover the in-plane direction with a maximum angle of 27.5° and the out-of-plane direction with a maximum angle of 38° . Since regular beam sizes are in the range of 0.1 mm, they bring rather strict requirements for the vertical and angular displacements of the sample table during spin-coating, therefore, our spinning system was optimized to have low deflection along the axial direction of the motor rod, some details on its development are discussed in Subsec. 4.2.1. The spin-coating procedure requires a remotely controlled liquid delivery system which is done by a micropipette mechanism. Antisolvent-assisted growth [72] and gas-quenching [143] are two common procedures that can be applied during spinning and both are supported in our compact environment. The atmosphere monitoring system consists of humidity and oxygen sensors placed at the height of the sample for precise measurements. The annealing system consists of a halogen lamp with a gold-coated reflector fixed to an adjustable mechanism and a pyrometer pointing at the sample surface. Visual control of the thin film deposition steps is provided by a camera targeted at the sample surface area and provides direct feedback regarding thin film solidification during spinning and annealing procedures. A technical drawing of the designed chamber and a photo of the spin-coating environment in operation at beamline P08 at DESY are shown in Fig. 4.1(b) Fig. 4.2, respectively.

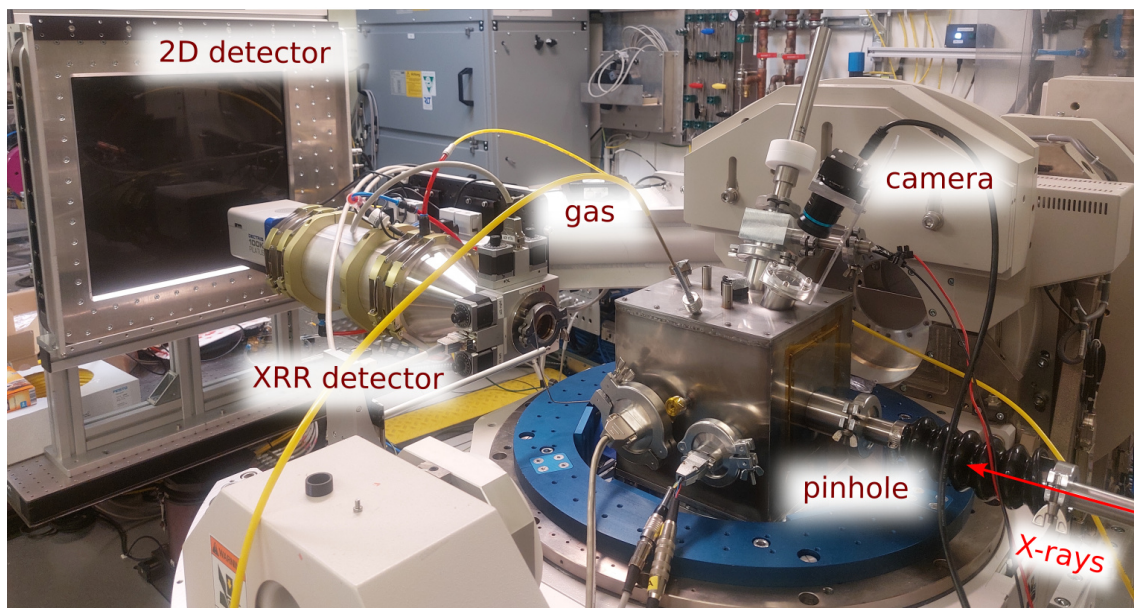


Figure 4.2.: Spin-coating chamber for *in situ* GIWAXS measurements, photos of the chamber in operation at beamline P08 [181] at DESY, setup for gasquenching-assisted method.

4.2. Chamber systems

In the current section all systems which the compact sample environment consists of are discussed in detail. The systems are the following: surveillance system, dispensing system, atmosphere control system, spinning system, annealing system, and DRS system.

4.2.1. Spinning system

The grazing incidence geometry brings certain limitations to the vertical (1) and angular (2) displacements of the sample table during rotation: (1) originates from the magnetic field of the motor, is reproducible, and can be corrected for prior to spinning, while (2) comes from the motor rod/sample table tilt and their vibration as well as backlash in the bearings. The optimization of (2) for the spinning system was carried out by choosing a stable in-runner motor, selecting the best geometry of the sample table, testing the screw configurations to fix the table to the motor rod: three M3 screws with angle of 120° between them should be used. The spinning system optimization process involved testing out different motors and corresponding motor housings, the intermediate results can be found in [188]. The motors tested are presented in Fig. 4.3, the results of stability tests are provided in Tab. 4.2.

The final spinning system consists of a motor DB42S02 from Nanotec fastened inside of a housing and a sample table (45 mm in diameter) fixed by three M3 screws on the rotating rod, substrates or samples can be attached by a heat-resistant sticky tape or silver paste. Since screw tightening induces some tilt, a counterforce has to be applied by pressing the



Figure 4.3.: Photos of the motors tested during spinning system development.

Table 4.2.: List of tested motors

Device	Observation	Datasheet source
EMAX RS2306 outrunner motor	Internal characteristics, such as rotor tilt, led to high wobbling amplitudes	[189]
DB28M01 inrunner motor	Stability not sufficient due to small motor housing and thin motor rod ($\varnothing 4$ mm)	[190]
DB42S02 inrunner motor	Excellent stability - bulky motor with thick motor rod ($\varnothing 5$ mm)	[191]

sample table while fixing each screw to keep the table surface flat. Besides that, screws should not be tightened as strongly as possible, since strong tightening induces a strong tilt. When both the sample table and the motor rod were marked, an optimal mutual configuration corresponding to the specific angle between the markings was found, resulting in a global "wobbling" minimum. The spin-coating motor is controlled by an Arduino *via* an electronic speed controller (ESC). The mapping values are being transferred to Arduino, processed by the **Servo** Arduino library, and being converted into the motor rotation frequency, which is defined by the ESC. The correlation between the mapping values and the motor rotation frequencies is shown in Fig. 4.4.

The static and periodic vertical displacements of the sample table were measured using a capacitive sensor D-510.101 PISeca from Physik Instrumente [192] placed close to the sample table. The change in capacitance is transformed into the change in sensor-to-sample table distance by the E-852 PISeca signal evaluation electronics [193]. Two types of vertical sample table displacement during rotation were measured: (a) static part and (b) periodic part in Fig. 4.5. Once spinning starts, the sample table is lifted by the magnetic force in the vertical direction. This value depends on the rotation frequency and goes up to $\sim 19.5 \mu\text{m}$. The periodic displacement amplitude, which originates from the tilt and vibration of the sample table, was measured at the edge of the sample table and in the center and is on average $5.5 \mu\text{m}$ and $2.5 \mu\text{m}$, respectively. The speed of 10000 rpm is the

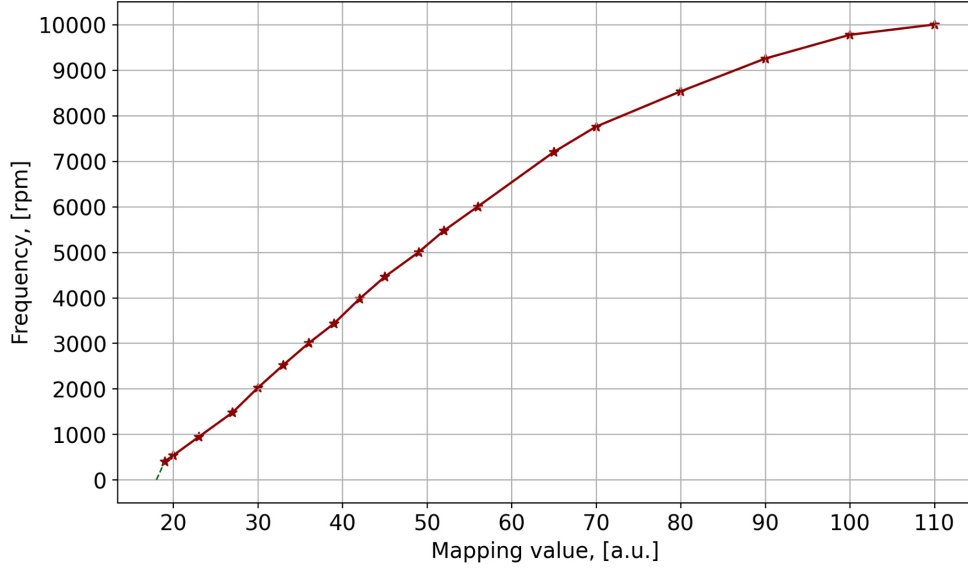


Figure 4.4.: The correlation between mapping values and motor frequencies for the motor at an operating voltage of 15 V.

maximum value supplied by the electronic speed controller, while 8000 rpm is the rated frequency up to which the motor is stable. The wobbling increase was always observed for speeds above 8000 rpm, this is directly related to the resonant frequency of the motor used [191]. Since the vertical size of the incoming X-ray beam is on the order of $\sim 100\mu m$, this wobbling will only slightly change the intensity due to the change in incident angle. The average angular displacement of the sample table of the spin-coater at frequencies up to 10.000 rpm is $\sim 0.01^\circ$ which is at least one order of magnitude smaller than typical angles of incidence for surface-sensitive GIWAXS.

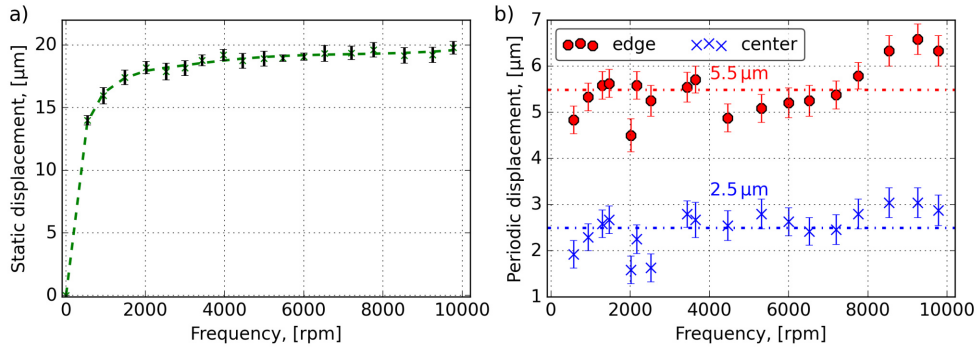


Figure 4.5.: The sample table vertical displacement amplitude: (a) static part which remains constant ($25\mu m$) from 4000 rpm up to 10000 rpm and (b) periodic part at the edge and center during each rotation of the sample table.

4.2.2. Dispensing system

Once the substrate is fixed on the sample table and the incoming X-ray beam is aligned, the precursor solution must be deposited. The dispensing system is very essential for remote solution delivery during X-ray scattering experiments. In the past, numerous different designs have been developed to remotely deliver specific amounts of liquids. Depending on the requirements for the specific application, one of two systems implemented into the setup can be used: syringe pump-based deposition or magnet-based micropipette pressing mechanism. Each of them is discussed separately, and the features and advantages of each system are highlighted.

Syringe pump-based liquid delivery

A syringe pump is widely used as a main tool for the delivery of solution [194] due to its flexibility: adjustable syringe diameter/dispensing rate, constant liquid flow, variability of connected tubing systems and remote control. The syringe pump used in the current research was AL-1000 from World Precision Instruments[195], the sketch is displayed in Fig. 4.6(a). It can be controlled manually by pressing buttons below the display or remotely using the RS232 communication protocol. One can choose a base syringe diameter, set the pumping direction (dispensing\withdrawing), pumping rate, volume to be dispensed and clear it, start\stop and perform master reset to set the default parameters.

The first designed geometry was suitable for antisolvent application, the base syringe had a volume of 60 mL, ensuring the fastest dispensing rate for this syringe pump. A brief representation of the experimental setup is shown in Fig. 4.6(a). Two tubes were connected to the syringe *via* the special connector: a long tube, directly connected to the syringe (upper part) and a short tube (lower part), ensuring that the material does not pass through the tube to the syringe, and the flexibility of the tube does not induce the drop of antisolvent earlier than necessary. Then, some antisolvent is loaded into the shorter part of the tube and inserted into the tube guide pointing at the sample surface area. This geometry was not ideal for antisolvent application, since it takes ~ 2 s to deliver ~ 150 μ L of the liquid, while time is a crucial parameter and ideally it should take ~ 200 ms to dispense antisolvent, since it allows the fabrication of highly efficient solar cells from a wide range of precursor stoichiometries [110]. It was empirically determined that such a rapid dispensation (~ 180 ms) can be achieved by using a 1000 μ L volume micropipette.

Magnet-based micropipette mechanism

A brief representation of the second geometry is shown in Fig. 4.6(b). As an alternative to the syringe pump-based antisolvent application method, a remotely controlled magnet-based mechanism was developed for pressing the micropipette. As mentioned above, the use of 1000 μ L volume micropipette is excellent for an antisolvent-based technique [110].

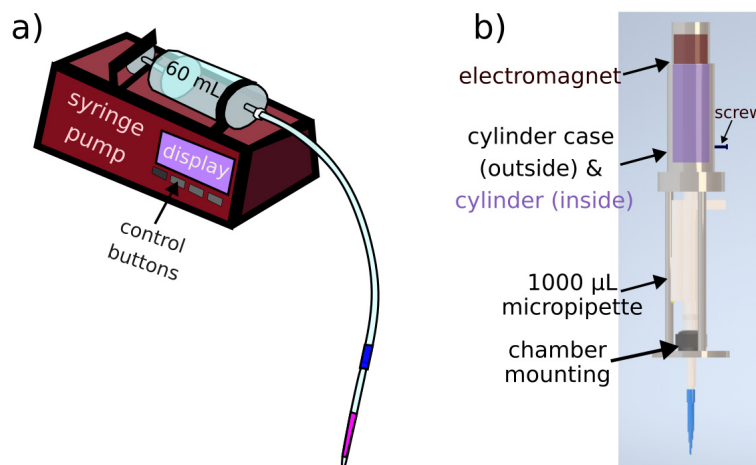


Figure 4.6.: Dispensing system realized within the chamber: (a) Syringe pump layout, used for antisolvent application. This setup offers high flexibility due to variable combinations of syringes and tubing systems; (b) Magnet-based micropipette pressing mechanism.

Keeping this in mind, the geometry, shown in Fig. 4.6(b) was developed. The electromagnet for locking doors was chosen to fulfill the task, as it is robust and reliable [196].

The working principle of this system is based on the presence of a rigid micropipette holder that ensures accurate pressing of its button by a cylinder inside of a cylinder case. A short RS232 command activates the electromagnet (on the top), and a cylinder inside a cylinder case can be moved up to stick it to the electromagnet. The solution delivery speed was estimated by recording an audio recording of a magnet turning off, leading to the sliding of the cylinder and pressing down the micropipette button and is approximately in a sub-100 ms range.

Typically, 40–60 μL of 0.4M to 1.4M perovskite precursor solution has to be delivered to the substrate prior to the spin-coating procedure. In this situation, the presence of heavy elements within the perovskite composition, such as lead, and the low viscosity of the precursor solutions (such as DMF and DMSO) make the use of tube-based systems, connected to the syringe pump, rather challenging. Small volumes of precursor solutions (40–60 μL) can be potentially delivered by 100 μL or 200 μL micropipettes without spontaneous drop.

In order to assist thin film crystallization, one-step conversion (OSC), antisolvent-assisted growth and gas quenching (Fig. 2.17) were implemented into our compact sample environment. Large volumes of antisolvent (150–250 μL) can be reliably delivered by a 1000 μL volume micropipette [110]. Gas-assisted thin film crystallization is supplied by placing a high-density polyethylene tube through the brass tube guide directed at the sample surface and controlled by the magnetic gas valve MHJ10-S-2,5-QS-6-HF electrically switched with an I/O output by DC signal in the range of 3–30 V [197].

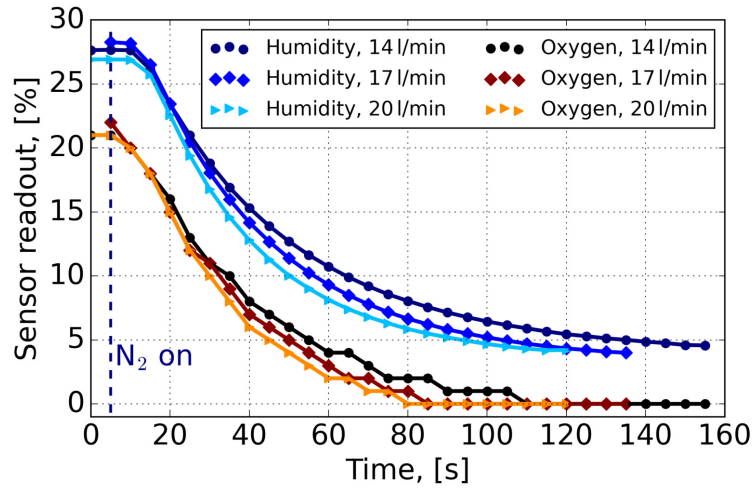


Figure 4.7.: Humidity and oxygen percentage measured with sensors placed inside of the chamber at the sample height. N_2 was switched on at 5 s of the experiments.

4.2.3. Atmosphere control system

Some thin films, such as perovskites, are typically grown in a nitrogen flushed glove box with low oxygen and humidity levels. The presence of an inert atmosphere within the compact sample environment is provided by inlets at the bottom and top of the chamber and is controlled by a B+B Sensors HYT939 humidity sensor [198] and an SGX Sensortech SGX-VOX oxygen sensor [199] at the sample level for more accurate measurements. Typical values of the percentage of humidity and oxygen after switching on different nitrogen flows can be seen in Fig. 4.7, which shows the drop in humidity from 27% to 5% and oxygen from 21% to 0% within ~ 120 s of nitrogen flushing at the latest. Such a fast achievement of working conditions is advantageous for the designed compact environment.

4.2.4. Annealing system

A spin-coating process often requires a subsequent annealing step; it is normally provided by transferring the spin-coated sample onto a hotplate (Fig. 4.8(a)). Since it would be technically challenging to implement a bottom-table annealing system to heat samples above 120°C without destroying the motor, which can withstand temperatures up to $\sim 80^\circ\text{C}$ [191], The alternative annealing system involves an infrared heater, installed above the coated film [32, 200–202]. In the current work, a halogen lamp with a near-infrared NIR spectrum was chosen. Essentially, the heat transfer mechanism for hotplate annealing and near-infrared annealing is different, which influences the nucleation rate and perovskite grain sizes. In the case of NIR annealed films, the short but intense heat flow provided to the organolead halide wet precursor *via* the fluorine tin oxide (FTO)- or ITO-coated glass substrate promotes substrate-driven nucleation and lateral growth of large crystals accompanied by an upward, vertical progression of solvent evaporation.

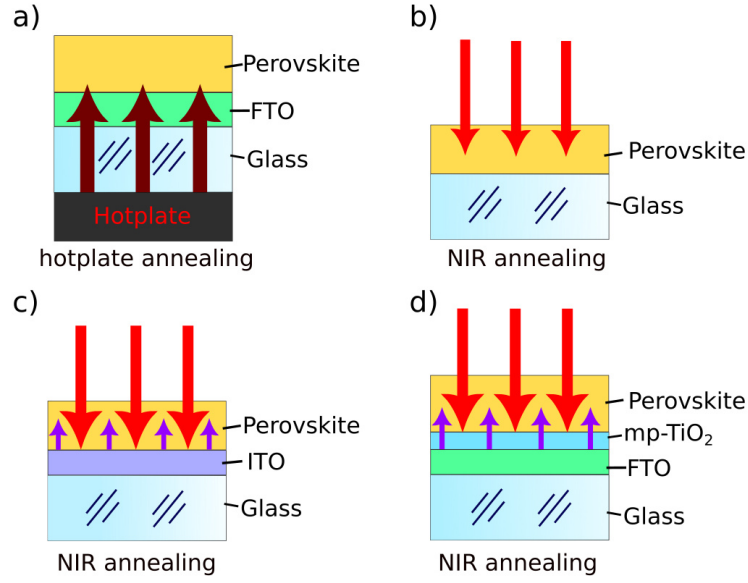


Figure 4.8.: A schematic representation of the differences between (a) hotplate annealing and NIR annealing applied to samples on (b) Glass, (c) Glass/ITO and (d) Glass/FTO/TiO₂ substrates. Colored arrows mean the direction of the heat: darkred - heat from the hotplate, red - lamp IR radiation, violet - reflected IR radiation.

Table 4.3.: Maximum operation temperature of the devices inside of the spin-coating chamber

Device	Maximum operating temperature	Datasheet source
oxygen sensor	+50°C	[199]
motor	+80°C	[191]
pyrometer	+125°C	[205]
humidity sensor	+125°C	[198]

Examples of using such an annealing mechanism with experimental details and results are summarized in Tab. A.1. Another way to induce crystallization of the deposited films is hot air quenching [203, 204], care should be taken to avoid any danger due to overheating of the motor used.

Due to the compact design of our chamber and strict limitations on the ambient temperatures of the devices used in the chamber (motor, humidity and oxygen sensors, pyrometer), summarized in Tab. 4.3, the annealing system was developed to have a targeted heat flow at the sample table. The heating system consists of a halogen lamp 64635 HLX from OSRAM [206] with a golden reflector that has a maximum power of 150 W and a color temperature of 3200 K attached to a custom-built magnet-based lamp mechanism with adjustable lamp-to-sample distance and connected to a power supply VOLTcraft

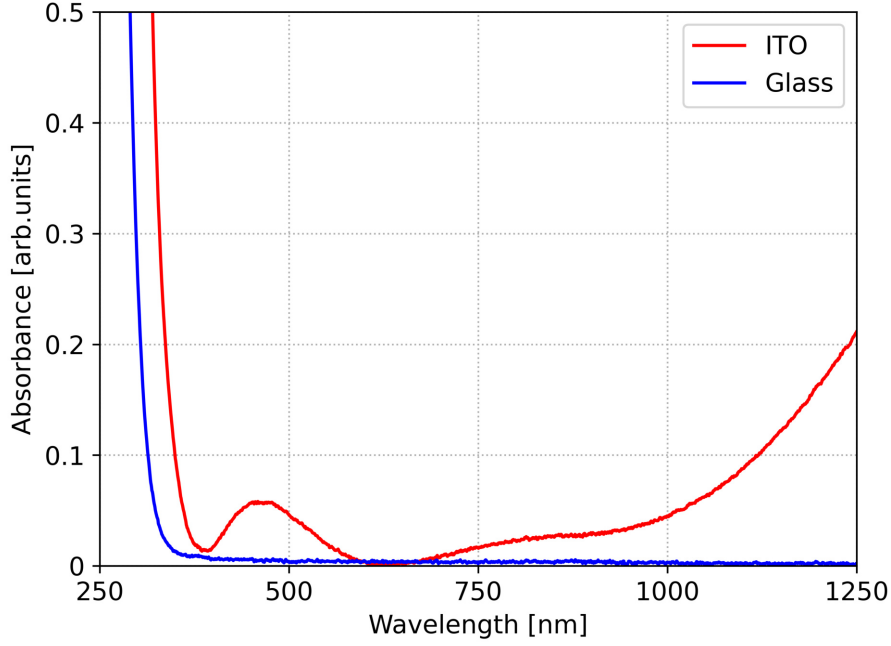


Figure 4.9.: Absorbance spectra of bare glass and ITO-coated glass substrates, used in current work for thin film deposition, measured by UV-Vis spectroscopy.

PPS-16005 [207]. Following Wien’s displacement law [208]:

$$(n\lambda T)_{max} = C_3 = 2898 \mu mK, \quad (4.1)$$

the wavelength of the maximum emissive power of the chosen infrared halogen lamp corresponds to:

$$(\lambda)_{max,lamp} = C_3 \approx \frac{2898 \mu mK}{3200 K} = 905.6 nm. \quad (4.2)$$

Since the sample table is made of aluminum, which exhibits a good reflectivity [200] for IR radiation (~ 0.98), motor is safe from being overheated even after longer exposure to the lamp at a power of 150 W.

The sample annealing procedure strongly depends on the substrate material, in [209] it is shown that the temperature of an FTO-coated glass is ~ 2 times higher (in $^{\circ}C$) than that of a bare glass substrate at the same NIR intensity (Fig. 4.8(b) and Fig. 4.8(d)). The typical substrates for spin-coating method of thin film photovoltaic materials are bare glass and indium tin oxide (ITO)-coated glass [210]. ITO is an important transparent conducting oxide and is composed of 90% indium oxide (In_2O_3) and 10% tin oxide (SnO_2) [210]. The absorption spectra of the bare glass and ITO-coated glass substrates are displayed in Fig. 4.9. It absorbs some UV, visible and IR light, thus serving as a heat reservoir that annealing the precursor solution from the bottom complementing direct heating by the lamp from the top (Fig. 4.8(c)). The addition of perovskite precursor material increases light absorption at lower wavelengths, compare the spectra corresponding to FTO and

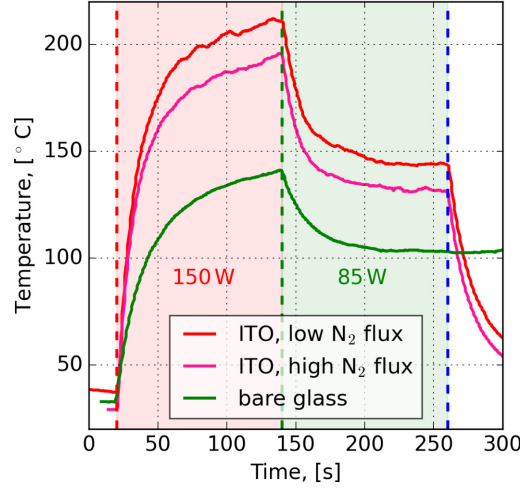


Figure 4.10.: Bare glass and ITO-coated glass temperature calibration performed by contact measurements using a thermocouple placed on substrate surface. Annealing parameters: lamp-to-sample distance of 40 mm, 120 s at 150 W and 120 s 85 W, typical for thin film fabrication. For ITO-coated glass, temperature at high nitrogen flow was estimated.

FTO+Perovskite precursor in Fig. A.2. Single-wavelength pyrometers are easy to use for the estimation of sample surface temperature, if its emissivity is known [211]. In our compact sample environment, the temperature of the sample surface is estimated by a pyrometer CT-SF15 from Micro-Epsilon with a small angle of view (15°) and a controller operated by RS232 interface [205]. The chosen pyrometer is sensitive to the far IR range $8\text{--}13\text{ }\mu\text{m}$. Because the emissivity of the sample varies during the annealing procedure because of the surface change from the precursor solution to the final film, this parameter in the pyrometer settings should be set to the target material emissivity for better precision.

The temperature calibration was performed by an estimation of the sample surface temperature using a K-type thermocouple connected to the UNI-T UT71D Digital Multimeter with a USB interface and a pyrometer targeted at the sample surface area [212]. The preliminary calibration was performed for the bare glass substrate and ITO-coated substrate with two different lamp powers: 85 W and 150 W at the lamp-to-sample distance of 4 cm, the geometry most applicable for *in situ* GIWAXS experiments; the result can be seen in Fig. 4.10. The maximum temperature for the bare glass substrate at low N₂ flow was 140°C , while for ITO-coated glass substrate it was 1.5 times higher, approximately 210°C . The N₂ flow reduced ITO-coated glass surface temperature by $\sim 10\%$. The annealing process can be determined by carefully selecting the nitrogen flow and the target annealing temperature. An additional improvement to the spin-coating chamber can be made by introducing a pressure sensor inside it to carefully reproduce the fabrication procedure, done inside a glovebox. In the present work, various compositions with different transformation temperatures were investigated; this information can be used to plan future

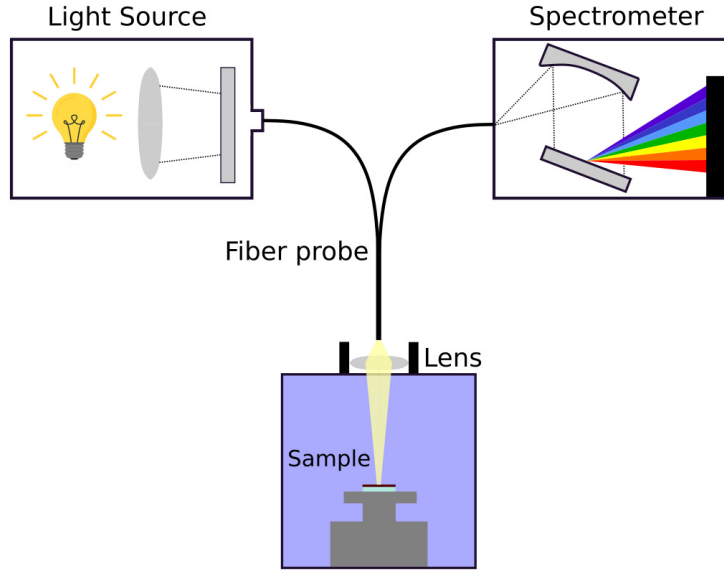


Figure 4.11.: A schematic representation of the differential reflectance spectroscopy working principle. A white light, generated by a Light Source gives a wideband signal, which is guided through the fiber probe and focused by a lens at the center of the sample, the probed area has a diameter of 1 mm.

annealing experiments.

4.2.5. Differential reflectance spectroscopy

For the *in situ* investigation of optical properties of perovskite thin films, the possibility of DRS measurements was included in the chamber. It was adapted to compact sample environment by Paul Zimmermann [213] and Niels Scheffczyk. The schematic representation of the DRS setup and the technical drawing of the designed system are presented in Fig. 4.11 and Fig. A.3, respectively. During the experiment, a white-light beam from a DH-2000 deuterium-tungsten halogen lamp [214] passes through the RP22 200 μm 0.22NA 250-1200 nm optical fiber [215] and is focused onto the sample's center area of 1 mm diameter using an Edmund Optics achromatic lens with a focal length of 8 cm [216]. Reflected light is detected by a USB2000+ charge-coupled device (CCD) from Ocean Optics [217]. The detector has an energy range of $E = 387\text{-}1100\text{ nm}$ and an optical resolution of $\Delta\lambda = 0.1\text{ nm}$. It is possible to record up to 1000 spectra every second.

As an example of DRS measurement, the growth of the typical perovskite MAPbI_3 composition was tracked during the gas quenching-assisted spin-coating process, and the result is presented in Fig. 4.12. By analyzing the thin film interference, measured by DRS, one can calculate the film thickness during spin-coating (Fig. A.4). The measurements showed a trajectory expected from the literature, since the resulting thickness depends on both the spinning speed and its duration [85]. With this method, the thickness could be

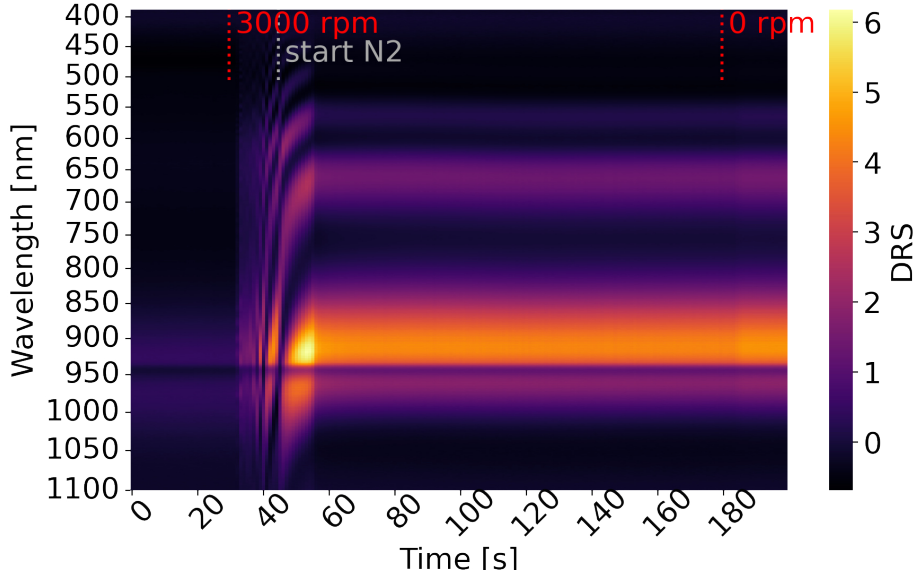


Figure 4.12.: DRS measurement during the spin-coating step. Dotted lines show the start and stop of the spin process and gas flow. At 30 s the motor starts spinning up to 3000 rpm. 45 s into the scan a nitrogen flow is directed at the sample [213].

measured in a range of $1\ \mu\text{m}$ to $22\ \mu\text{m}$. The upper limit is due to noise, and the lower limit is due to the limited spectral range. Depending on the conditions of the sample, the DRS signal can also be used to model the absorption coefficient of the sample during preparation. The intense peak around 905.6 nm, observed within the DRS spectra during the annealing procedure, corresponds to the maximum of the halogen lamp, used for heating.

4.2.6. Surveillance system

The thin film deposition process is controlled by a surveillance system, based on a high-quality (HQ) PiCamera mounted on the upper flange of the spin-coating chamber, which is shown in Fig. 4.2. The HQ PiCamera captures detailed and colorful videos with high resolution [218], indicating the formation of thin films from liquid solvents through spin-coating and annealing steps. An exemplary mixed-halide 3D perovskite thin film deposition by the N_2 -assisted gas-quenching method is shown in Fig. A.5, which shows how gas treatment initiates the conversion of the precursor solution to the solid perovskite phase. The color of the thin film changes due to the phase conversion leading to the change in optical properties, for example: from yellow to black (MAPbI_3 and FAPbI_3 compositions), from transparent to orange (MAPbBr_3 composition) and from light yellow to red/orange (2D perovskite compositions). These color changes are well known and characteristic for the studied perovskites and are described elsewhere [219, 220].

4.3. Software infrastructure

This section displays the software system that compliments the designed chamber by controlling all the embedded devices. The spin-coater setup consists of different devices and its communication diagram is shown in Fig. 4.13. The central part represents the TANGO device servers running on a Raspberry Pi 4 [221] with all connected devices, where TANGO is a free open source device-oriented controls toolkit. This feature makes our spin-coater software compatible with synchrotron facilities using TANGO and allows the device to be controlled from the main beamline control computer and within the beamline control software (e.g. Spock/Sardana at P08 of PETRA III/DESY, Hamburg). The spin-coating motor is controlled by an Arduino *via* an electronic speed controller (ESC). The micropipette mechanism with the magnetic switch, humidity, and oxygen sensors are controlled by a second Arduino. The dispensing mechanism is triggered by switching off the electromagnet; the humidity sensor HYT 939 from Conrad Electronic [198] is communicating *via* I²C protocol whereas the oxygen sensor [199] generates an output voltage signal transformed into an oxygen level in %. The annealing system consists of a pyrometer [205], halogen NIR lamp [206] and a lamp power supply [207], both controlled *via* RS232 communication.

Since all systems within the designed chamber have to be remotely controlled from a main computer, it was realized by creating a graphical user interface (GUI) (Fig. 4.14) and alternatively creating a macro in Python, which can be run in terminal. The temperature of the sample surface, estimated by the pyrometer, is saved in the metadata files and can be easily extracted later during the data analysis. For a more precise estimation, the emissivity of the object can be set by sending the appropriate command to the pyrometer.

4.4. Chamber infrastructure

The spin-coating chamber assembly can be divided into two parts: the first part includes the preparation and mechanical assembly of all parts, shown in Fig. 4.15. The second part represents the assembly of the electronic devices used, displayed in Fig. 4.16.

1. Place kapton foil on the scattering window; in the case of using chemicals, secure the inside part of the chamber with heat-resistant foil around the motor and avoid its contact with the sample table. This ensures an easier cleaning procedure and secures both sensors.
2. Fix the adapter plate to the Kohzu diffractometer with long screws and necessary spacers. The adapter plate is fixed by the 4 M5 screws to Kohzu diffractometer. Then, the spin-coating chamber can be placed on the top of the adapting plate and fixed by the four screws with a ball tip which ensures tight fixation.

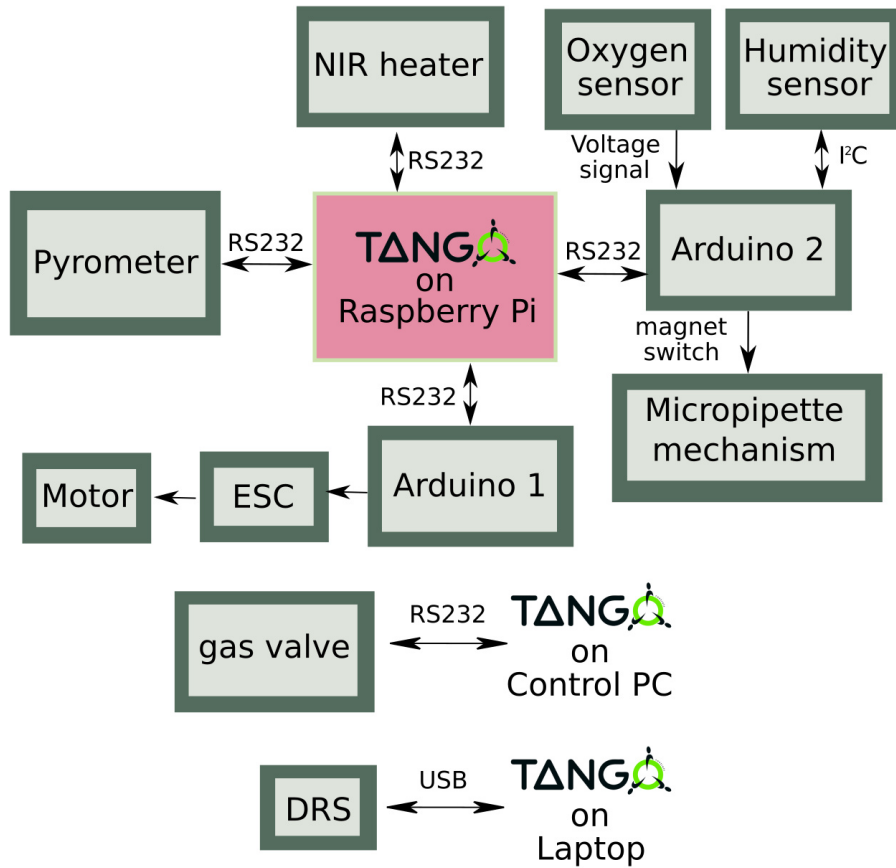


Figure 4.13.: Communication diagram of the spin-coater devices controlled *via* PyTANGO installed on Raspberry Pi 4. NIR heater and Pyrometer are directly controlled by RS232 serial communication; ESC running the motor is controlled *via* Arduino 1; All other devices are controlled by Arduino 2: Humidity Sensor uses I²C protocol, Oxygen Sensor gives a Voltage signal proportional to oxygen level and the Micropipette mechanism is triggered by a 12 V signal. Gas valve is controlled *via* RS232 by TANGO server on the Control PC. DRS is controlled *via* USB by TANGO server installed on a Laptop.

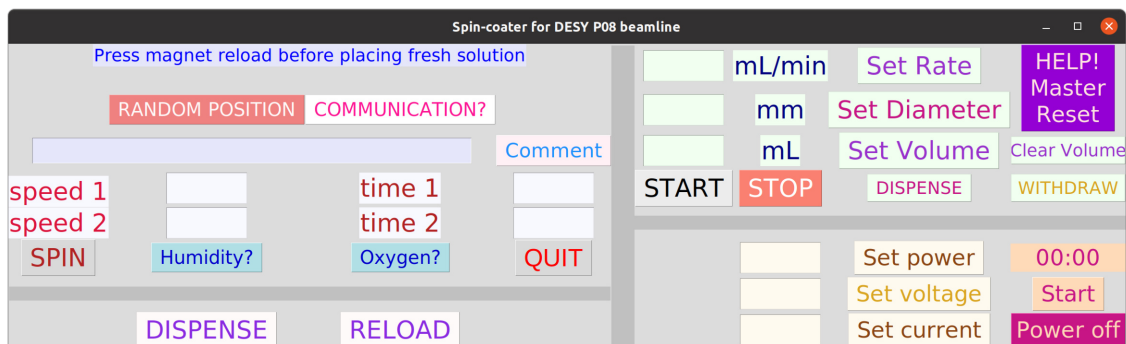


Figure 4.14.: GUI with features for controlling most of the systems within the compact sample environment. The left side controls the spin-coating and micropipette fluid delivery mechanism, and can also be used to control humidity and oxygen levels in the chamber. The right part is responsible for syringe pump (top) and NIR halogen lamp (bottom).

3. Adjust the pyrometer position to ensure that the sample is in the field of view.
4. Secure humidity and oxygen sensors inside of the 3D printed chemical-resistant cases and fix them at the sample height.
5. Fix the camera holder on the window flange with 6 screws.
6. Fix the camera on the camera holder and adjust the lens.
7. Fix the lamp mechanism on a flange on the top lid using a flange connector with a robber gasket inside for a tight connection.
8. Plug-in golden reflector halogen lamp. The closest lamp-to-sample distance ensures the best performance for thin film annealing.
9. Connect control cables according to the assembly scheme, shown in Fig. 4.15.
10. Connect and install the micropipette pressing mechanism (for the antisolvent-assisted method).
11. Insert a brass tube guide and gas tube (for the gas-quenching method).
12. Run TANGO device servers and launch GUI from command line, the resulting window is displayed in Fig. 4.14.
13. Connect to the Raspberry Pi with Pi Camera and launch the surveillance stream.
14. Prepare a macro with predefined spin-coating\annealing sequence, synchronized with X-ray scattering measurements.

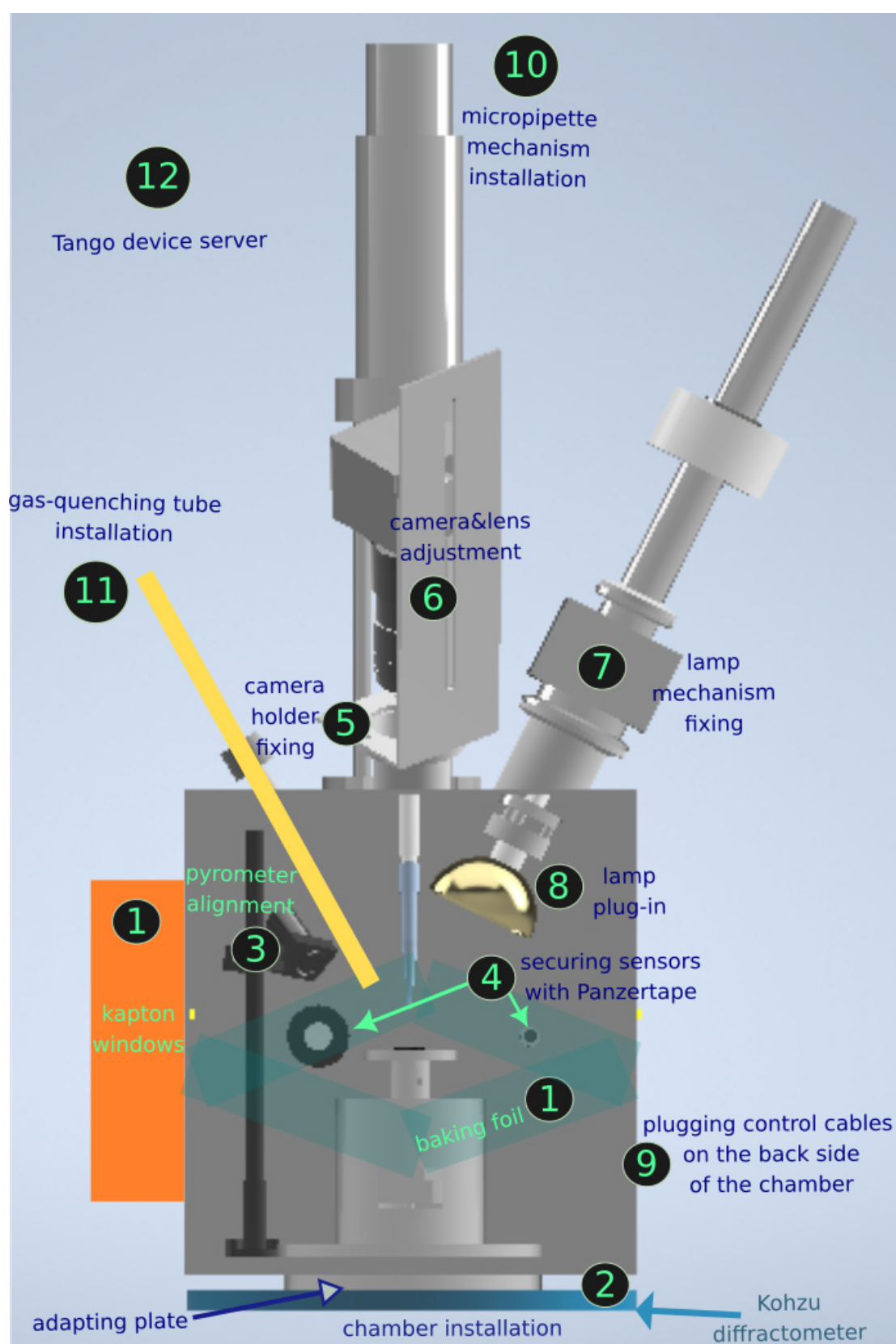


Figure 4.15.: The assembly order of the spin-coating chamber before starting its operation.

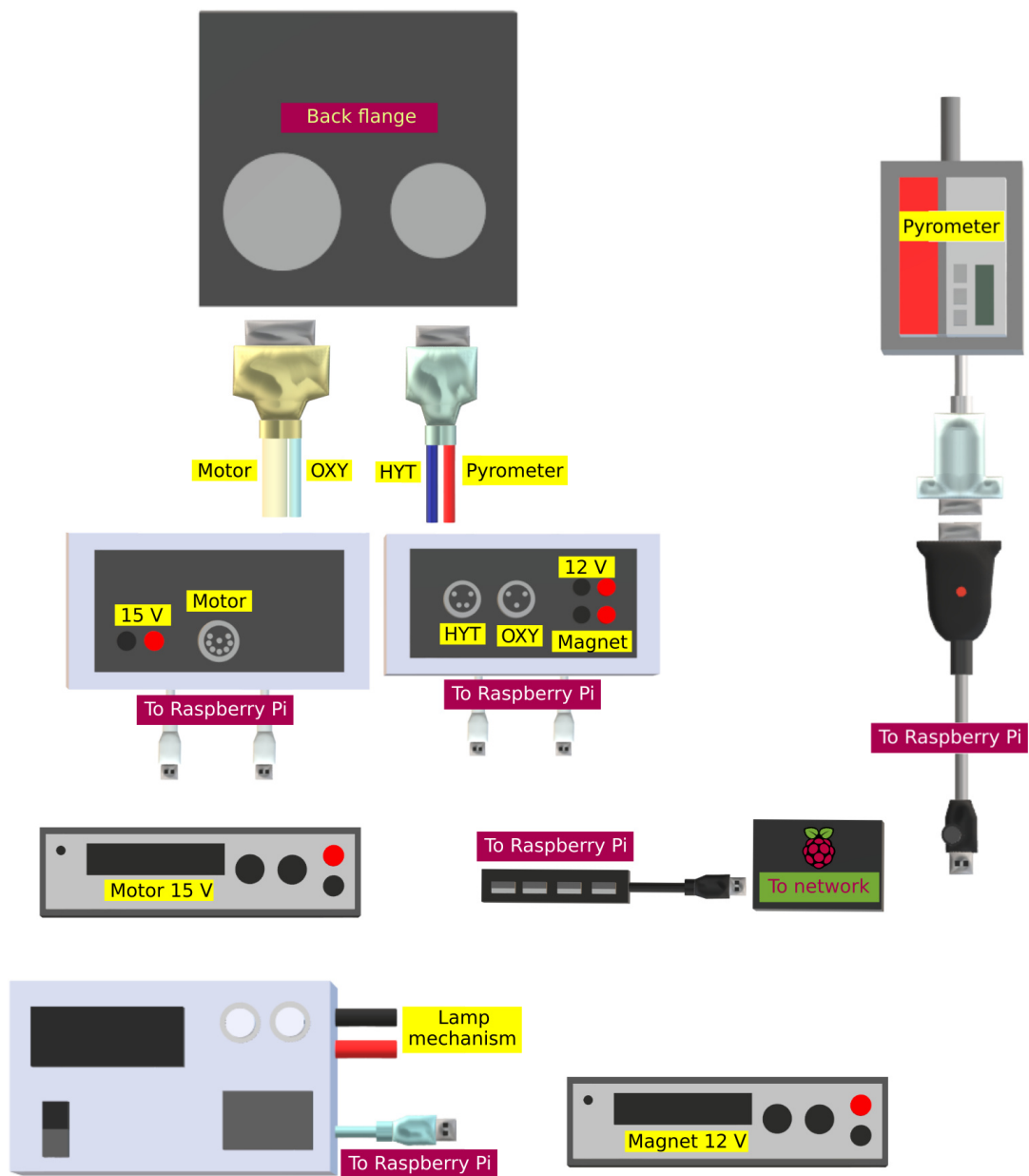


Figure 4.16.: Spin-coating chamber assembly: all major devices are displayed with corresponding connectors and labels.

4.5. Supporting devices

During the development of the compact sample environment, two devices were used as additional tools: for the spinning system a capacitive sensor was used, while the annealing system could benefit from using a thermopile array of 80x64 pixels.

4.5.1. Capacitive sensor

Monitoring of the sample table wobbling originating from (i) internal motor characteristics and (ii) the quality of the sample table fixing was done by the capacitive sensor. The technical realization of the experimental geometry is shown in Fig. A.6. In the sketch, the capacitive sensor held by a holder is fixed on an optical table next to the spinning system, consisting of a spinning motor, motor housing, and sample table. For a more complete characterization, the displacement values were measured in the center and on the edge of the sample table. The distance between the capacitive sensor and the sample table was adjusted using a micrometer positioning screw. The capacitive sensor measurement range is equal to the minimum distance between the sensing element surface and the surface of the sample table. To achieve higher precision, the sensor must be placed in the middle of the measurement range, indicated by the LED on the PISeca signal evaluation electronics tableau [193]. Such geometry ensures the best performance, since in this range linearity of the sensor is provided.

4.5.2. Thermopile array

Estimation of the temperature distribution of the designed annealing system was performed using the Heimann HTPA thermopile array [222] with the size of 80×64 pixels. This array was mounted inside a housing fixed to the universal holder, shown in Fig. 4.16, which can also be used to hold the Pi camera [218]. Thermopiles are thermal detectors that convert incident radiation into a temperature rise. This temperature change is measured through either one or more thermocouples or by using the pyroelectric effect. A single, usually blackened (to increase absorption) thermocouple is the simplest and cheapest of all thermodetectors. However, a single thermocouple suffers from high amplifier noise and therefore limited detectivity. Thermopile detectors can be manufactured through thin-film processes as a set of n miniature thermocouple junctions (20 to 120), connected in series as differential pairs [223]. The hot and cold junctions are connected by two different materials with large thermoelectric power and opposite polarities, called "arms", creating a Seebeck effect between the junctions [224]. For silicon thermopiles, the "arm" materials can be alternating n-type and p-type poly silicon. The cold junctions are then thermally connected to the detector package and are located around the perimeter of the substrate opening [223]. The hot junctions are located in the center of the detector pattern and are coated with an energy absorber. The hot junctions define the active area of the detector and are suspended on a thin membrane that is thermally isolated from the rest of the

package. To make a radiometrically calibrated measurement with a thermopile detector, the detector cold junction temperature must be known. This is typically accomplished by measuring the temperature of the detector package using a built-in thermocouple. The selected thermopile array has an embedded thermocouple that measures the detector package temperature and allows data correction [222]. The thermopile array was connected to the Raspberry Pi 3 [225] and controlled *via* serial peripheral interface (SPI), a common interface for embedded systems to facilitate short-distance communication. The object and ambient temperature could be calculated from the stored calibration data and the sensor output. This included careful consideration of all the corrections for the following conditions: ambient temperature (as discussed above), thermal offset (compensation for any thermal drifts), electrical offset (compensation for any changes in the supply voltage), supply voltage compensation, pixel sensitivity compensation and object emissivity, and the resulting object temperature is then calculated by using a look-up table and doing a bilinear interpolation. Due to the complexity of the intermediate steps on the way to the final result, only an overview of the internal memory of the thermopile array is presented in Fig. A.7, which includes various values/matrices stored as different data types. The communication code was written in Python which included accessing the internal memory and implementing all the corrections.

Due to the wide-wavelength response, the surface of the observed object should not reflect, since the array assumes that the detected radiation is exclusively blackbody radiation. This array was first used for testing the heat distribution, caused by the lamp, used for the sample annealing. Before the halogen lamp was installed, a ceramic heater was used for sample annealing, but it caused excessive overheating of the chamber because the heat flow was not focused exclusively on the sample. As a result, the annealing procedure initiated sample misalignment due to thermal expansion of the sample table, made of aluminum. This problem was solved by using simultaneously three temperature measuring devices to calibrate the effect of sample annealing on chamber temperature [188], namely pyrometer [205], K-type thermocouple, connected to multimeter [212], and a thermopile array [222], directed at the chamber wall, covered with a plastic foil.

In order to find the most appropriate and highly efficient annealing procedure, a square ceramic plate with a size of 50×50 mm was placed on the top of the sample table, which has a diameter of 45 mm. The geometry of the experiment is shown in Fig. 4.17(a). The ceramic plate was covered with baking foil, which has an emissivity of ~ 0.95 , which ensures a more precise estimation by the array. The temperature distribution was measured using the geometry most applicable for beamtimes: at the closest distance between the lamp and the center of the sample table of 40 mm. The efficiency of lamp-induced heating was studied depending on the rotation of the lamp mechanism. For this purpose, three different positions were chosen with an angle of 120° between them, based on the screws on the lamp-holding rod, and are referred to as 1, 2 and 3. Each time, the annealing procedure was done at a lamp power of 85 W for 190 s. For calibration purposes, a pyrometer

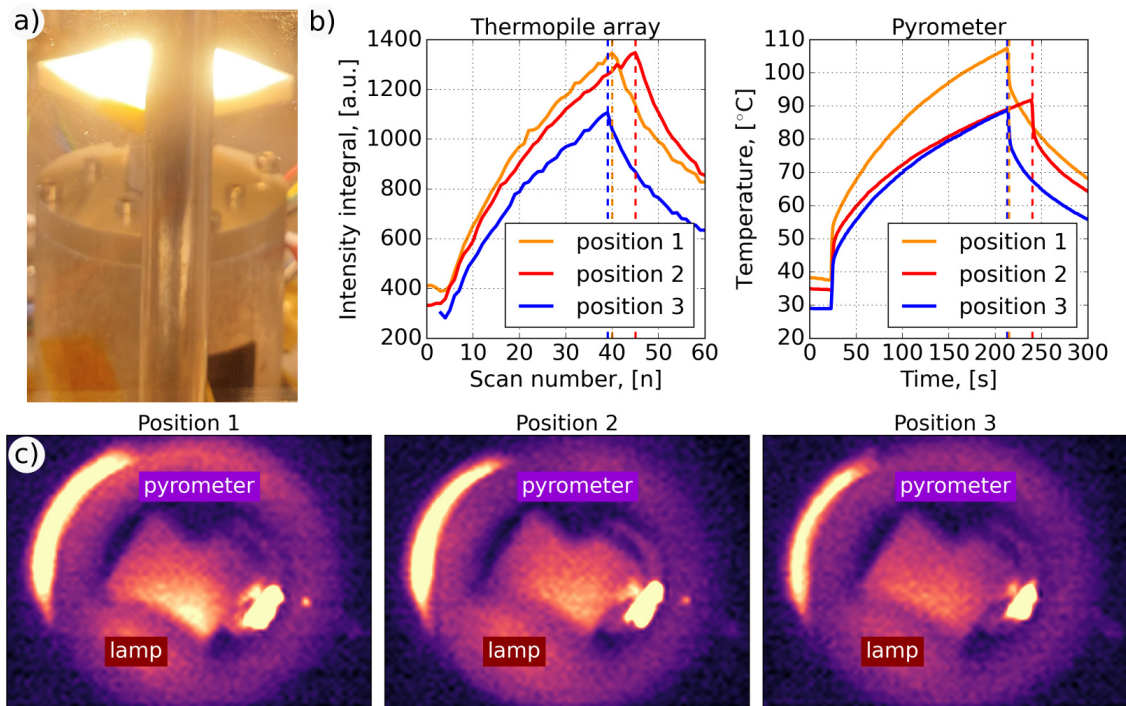


Figure 4.17.: Calibration with annealing at different lamp positions: (a) photo of the geometry; (b) integrated profiles extracted from (c) annealing scans measured by the HTPA thermopile array (1 scan ~ 5 s) and temperatures estimated by the pyrometer. Average annealing time was 190 s.

that was aimed at the center of the ceramic plate was used. The intensity detected in the center of the ceramic plate was integrated over time. The results of the optimization of the position of the lamp mechanism are shown in Fig. 4.17. The position marked as **1** gives the most optimal annealing geometry, leading to the fastest annealing process. This configuration was then used for the annealing of thin films.

4.6. Conclusions from this chapter

The designed chamber, described in detail in the current chapter, was tested during at least 10 beamtimes at DESY and ESRF synchrotron facilities, and already provided various essential insights into perovskite crystallization kinetics, which would not be possible without *in situ* grazing-incidence X-ray scattering measurements. Meeting strict requirements and optimizing this device to serve as a robust unit of infrastructure was the main goal of the current work. The spinning system ensures reliable spin-coating procedure, while NIR halogen lamp annealing completes thin film crystallization, and the sample surface temperature is estimated by the pyrometer. Additional systems, including the magnet-based antisolvent application tool, the gas valve and atmosphere control system with humidity and oxygen sensors, ensure a precise thin film deposition procedure. The film transformation can be tracked by the surveillance system, based on the high-resolution camera with the appropriate lens.

A big step in software development was made by transferring the device control from the developed Python-based GUI to TANGO, which is robust and compatible with the synchrotron infrastructure, allowing remote control of the implemented systems and adding them to executable macro commands that can be run from the control computer.

Most of the data, acquired with the help of the designed chamber, have not yet been published, but some of the published articles can already show its performance [36–39]. The next two chapters include some of the *in situ* scattering data from different perovskite structures, analyzed by the author of this thesis, including 3D compositions (Chap. 5) and 2D compositions (Chap. 6).

5. 3D perovskite crystallization data

5.1. Introduction

The previous chapters introduced the interest of studying crystallization kinetics of hybrid organic-inorganic materials and described the compact sample environment developed for *in situ* X-ray scattering characterization of materials during spin-coating[36]. The goals of this chapter are to resolve the complexity of crystallization pathways observed in some 3D perovskite compositions and to demonstrate the performance of the designed spin-coating chamber. The compositions in the scope of the research feature one to four cations (MA^+ , FA^+ , Cs^+ , Rb^+) and one to two halides (I^- , Br^-). The exact list of compositions studied, with the numbers of the corresponding subsections, can be found in the Tab. 5.1. The perovskite precursor solutions were deposited by three different methods: conventional one-step conversion (OSC), antisolvent-assisted method and gas quenching. The first column in Tab. 5.1, OSC (anneal), corresponds to the films, deposited in a commercially available spin-coater and measured with *in situ* X-ray scattering during the hotplate annealing experiment, carried out at the ID10 beamline of the ESRF. The other three columns represent the experiments, carried at P08 beamline [181] of DESY, and included X-ray scattering experiments during spin-coating and annealing of the samples, produced in the spin-coating chamber.

The studied samples can be divided into four groups, depending on the method applied. All films were deposited by the four different methods, the subsection numbers are displayed in Tab. 5.1.

5.2. Multication perovskite crystallization during one-step deposition

When utilizing the one-step method, disentangling crystal formation mechanisms are complicated due to the influence of processing parameters on one another. The morphological features observed by GIWAXS methods might not be necessarily straightforward and independent [226]. Nevertheless, in the current chapter these mechanisms are scrutinized for the compositions with one to four cations: single cation MAPbI_3 , FAPbI_3 , MAPbBr_3 and CsPbI_3 compositions; double cation composition $(\text{FAPbI}_3)_{0.83}(\text{MAPbBr}_3)_{0.17}$ referred to as FA:MA; triple cation composition FA:MA:Cs (95% FAMA with 5% CsI) and quadruple cation composition FA:MA:Cs:Rb (95% FA:MA:Cs with 5% RbI) in real-time by *in situ*

Table 5.1.: Structural composition of the studied samples during four different deposition methods with subsection numbers. OSC (anneal) corresponds to hotplate annealing experiment. The other three columns, namely OSC (spin & anneal), Antisolvent and Gas, represent experiments done in the compact sample environment during spin-coating by three different methods and annealing done with halogen lamp.

Composition	OSC (anneal)	OSC (spin & anneal)	Antisolvent	Gas
MAPbI ₃	5.2.3	5.5.2	5.6.1	5.8.1
FAPbI ₃	5.2.4	5.5.1	5.6.2	5.8.2
FAPbI ₃ in DMF	—	5.4.1	5.4.2	5.4.3
MAPbBr ₃	5.2.5	5.5.3	5.6.3	—
CsPbI ₃	5.2.6	—	—	—
FA:MA	5.2.9	5.5.4	5.6.5	5.8.3
FA:MA:Cs	5.2.10	5.5.5	5.6.6	5.8.4
FA:MA:Cs:Rb	5.2.11	—	—	—
(MAPbI ₃) _{0.95} (CsI) _{0.05}	—	5.7.1	5.7.3	—
(FAPbI ₃) _{0.95} (CsI) _{0.05}	—	5.7.2	5.7.4	—
(MAPbBr ₃) _{0.95} (CsI) _{0.05}	—	5.7.5	5.7.6	—

Composition	One step conversion (anneal)	One step conversion (spin & anneal)	Antisolvent	Gas-quenching
MAPbI ₃	(MA) ₂ Pb ₃ I ₈ ·2DMSO	(MA) ₂ Pb ₃ I ₈ ·2DMSO	IPA intermediate, (MA) ₂ Pb ₃ I ₈ ·2DMSO	(MA) ₂ Pb ₃ I ₈ ·2DMSO
FAPbI ₃	FAPbI ₃ ·DMF, 2H	2H	FAI-PbI ₂ ·xDMF, 2H	2H
FAPbI ₃ in DMF	-	(FA) ₂ Pb ₃ I ₈ ·4DMF, FAPbI ₃ ·2DMF, FAPbI ₃ ·DMF, 2H	(FA) ₂ Pb ₃ I ₈ ·4DMF, FAPbI ₃ ·2DMF, FAPbI ₃ ·DMF, 2H	(FA) ₂ Pb ₃ I ₈ ·4DMF, FAPbI ₃ ·2DMF, 2H
MAPbBr ₃	perovskite	perovskite	perovskite	-
CsPbI ₃	δ-CsPbI ₃	-	-	-

Figure 5.1.: The list of intermediate phases between the precursor solution and final perovskite films for single cation compositions produced by different methods. OSC data (anneal) is shown in Sec. 5.2. OSC data (spin & anneal) is shown in Sec. 5.5. Antisolvent-assisted data is shown in Sec. 5.6. Gas quenching data is shown in Sec. 5.8. FAPbI₃ in DMF is shown in Sec. 5.4 as an additional research on FA- and DMF-based intermediate phases.

GIWAXS, a common technique for revealing perovskite thin film growth kinetics [28–30, 37, 227].

This section demonstrates the crystallization pathways of perovskite compositions from deposited solutions to the final films, extracted by combining GIWAXS measurements

Composition	One step conversion (anneal)	One step conversion (spin & anneal)	Antisolvent	Gas- quenching
FA:MA	$(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$, DMF-based, 2H, 4H, 6H	4H, 6H	$\text{FAI-PbI}_2 \cdot x\text{DMSO}$, DMF-based, $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$, 2H, 4H, 6H	2H, 4H, 6H
FA:MA:Cs	$(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$, 4H	4H	$\text{FAI-PbI}_2 \cdot x\text{DMSO}$, $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$, 4H, $\delta\text{-CsPbI}_3$	4H
FA:MA:Cs:Rb	$\delta\text{-CsPbI}_3$, 4H	-	-	-
$(\text{MAPbI}_3)_{0.95}(\text{CsI})_{0.05}$	-	$(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$	$(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$	-
$(\text{FAPbI}_3)_{0.95}(\text{CsI})_{0.05}$	-	2H	IPA intermediate, $\text{FAI-PbI}_2 \cdot x\text{DMSO}$, 2H	-
$(\text{MAPbBr}_3)_{0.95}(\text{CsI})_{0.05}$	-	perovskite	perovskite	-

Figure 5.2.: The list of intermediate phases between the precursor solution and final perovskite film for mixed cation compositions produced by different methods. OSC data (anneal) is shown in Sec. 5.2. OSC data (spin & anneal) is shown in Sec. 5.5 and Sec. 5.7. Antisolvent-assisted data is shown in Sec. 5.6 and Sec. 5.7. Gas quenching data is shown in Sec. 5.8.

before, during and after annealing. A solvent complex $\text{FAPbI}_3 \cdot \text{DMF}$, not observed before, was identified for compositions with a major fraction of FAPbI_3 . The increasing number of cations within the composition resulted in faster perovskite phase growth and made coherently scattering island sizes larger. For compositions with two and more cations an important role of the 4H hexagonal phase in thin film crystallization was revealed. The addition of Cs^+ into the precursor solution led to two-step growth of Cs-containing phases which might indicate its high ability to Form crystallizes within the deposited solution prior to annealing.

For a comprehensive overview of the effects which different cation mixtures in the perovskite composition can have on film structure and crystallization, various mixtures were studied. The exact mixing ratios and solvent compositions are given in Tab. 5.2. To begin with, single cation compositions, i.e. simple lead halide perovskite materials employing one cation and one halide, are discussed and compared. Afterwards, the effects of mixing organic cations FA and MA and halides I and Br as well as adding inorganic cations (such as Cs^+ and Rb^+) will be discussed.

5.2.1. Experimental details

X-ray scattering experiments were performed at the beamline ID10 of ESRF with a photon energy of 22 keV. The scattering geometry is shown in Fig. 5.3(c): the sample to detector distance was 295 mm and the beam size was $15 \mu\text{m}$ in vertical direction and $140 \mu\text{m}$ in

Table 5.2.: Structural composition of the studied samples and solvents.

Sample	Solvent	Substrate
MAPbBr ₃	DMF	Glass/FTO/TiO ₂
FAPbI ₃	DMF	Glass/FTO
CsPbI ₃	DMF	Glass/FTO/TiO ₂
MAPbI ₃	DMF:DMSO (1:1)	Glass/FTO
FA:MA	DMF:DMSO (4:1)	Glass/FTO
FA:MA:Cs	DMF:DMSO (4:1)	Glass/FTO
FA:MA:Cs:Rb	DMF:DMSO (4:1)	Glass/FTO

horizontal direction. The angle of incidence α_i for *in situ* GIWAXS was 0.14° , while the integration time per image was 1 s. Additionally, *ex situ* GIWAXS patterns with different angles of incidence ($\alpha = 0^\circ$ – 0.2° with 0.02° steps) were measured before and after annealing treatment, to assess variations between surface and bulk structures. GIXD scans at the angle of incidence $\alpha_i = 0.14^\circ$ were recorded by a point detector for each sample in order to probe the in-plane crystal structure and scattering domain sizes with higher resolution.

5.2.2. Single cation samples

The following sections are focused on the crystallization kinetics of single cation compositions, namely MAPbI₃, FAPbI₃, MAPbBr₃ and CsPbI₃. A perovskite film production involves deposition of the precursor solution, followed by the annealing procedure, resulting in a successive crystallization process. Depending on the A-site cation and halide, used in the composition, the coated films either form various intermediate phases or crystallize directly as a perovskite phase.

5.2.3. Methylammonium lead iodide

One of the first and most investigated perovskite compositions is MAPbI₃, which demonstrated suitable optical properties to be used as a light sensitizer in organic-inorganic photovoltaic devices [123]. MAPbI₃ was observed to crystallize *via* conversion of a solvent complex intermediate structure. Based on the position of Bragg peaks in the GIWAXS data of MAPbI₃ before annealing (Fig. 5.4(a)), the (MA)₂Pb₃I₈·2DMSO solvent complex was identified with its reflections located at $|q| = 0.45 \text{ \AA}^{-1}$, $0.51 \text{ \AA}^{-1}$ and $0.65 \text{ \AA}^{-1}$ corresponding to (002), (021) and (022) planes, respectively [152]. Besides that, the scattering data suggested the presence of a small amount of lead iodide [228] (PbI₂) with its reflection at $|q| = 0.9 \text{ \AA}^{-1}$.

The subsequent annealing resulted in a simultaneous increase of the DMSO-based phase intensity and the decrease of the PbI₂ Bragg intensity, lasting ~ 30 s (Fig. 5.4(c)). This indicates thermally-induced formation of the DMSO-based solvent complex, which is stable [229] up to 70°C . The annealing procedure led to the full conversion of the DMSO-based

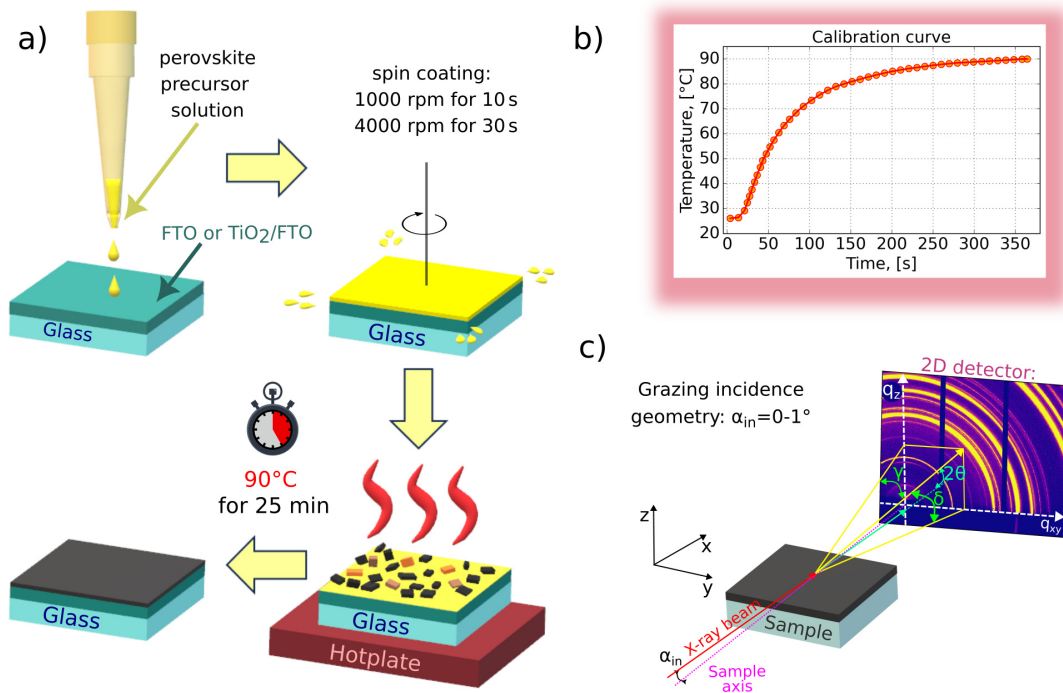


Figure 5.3.: Schematic of the experiment: (a) Corresponding perovskite precursor solution was spin-coated at 1000 rpm for 10 s followed by 4000 rpm for 30 s, then the film was placed on the annealing stage on the diffractometer and characterized by GIWAXS before, during and after the annealing procedure; (b) A calibration curve measured by a thermocouple showing the sample temperature during the annealing procedure and *in situ* GIWAXS. The sample was annealed with a hotplate, temperature of 90°C was achieved within ~ 300 s; c) Grazing incidence scattering geometry for observing crystallization process.

intermediate phase into the cubic perovskite phase after ~ 350 s of heat treatment (1 $\rightarrow$ 2) visible by the simultaneous decrease of intermediate phase intensity and increase of the perovskite signal (Tab. 5.3). Along with the perovskite phase, an increase in intensity from PbI_2 was detected. This might originate from the prolonged heating, since the annealing at 90° for 5 min was reported to be optimal [229], while in the current experiment it was done for ~ 24 min, and resulted in partial decomposition of the perovskite material [230, 231]. The raw *in situ* GIWAXS data during thermal annealing with marked structures is displayed in Fig. B.3(a).

The GIWAXS data of the final film, presented in Fig. 5.4(b), suggests that both perovskite phase and PbI_2 were present after annealing. Both of the phases were evenly distributed throughout the whole thin film, since they had a similar intensity dependence on the angle of incidence of the probing X-ray beam (Fig. B.1). The molar phase fraction of PbI_2 in the final film was 26% (Fig. 5.9). The resulting tetragonal perovskite phase of MAPbI_3 [232] was observed with its characteristic (040) reflection located at $|q| = 1.65 \text{ \AA}^{-1}$ within the cooled sample, since cubic-to-tetragonal phase transition takes

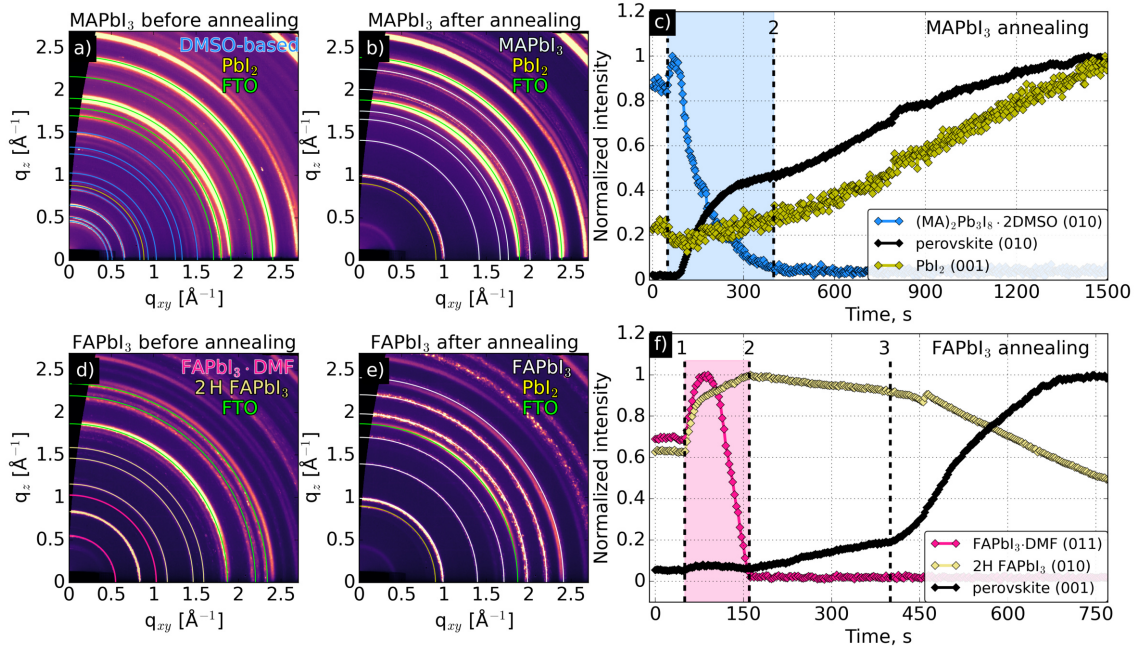


Figure 5.4.: GIWAXS of MAPbI₃ and FAPbI₃ perovskite films at the angle of incidence $\alpha_i = 0.2^\circ$ with marked structures: MAPbI₃ with PbI₂ and (a) (MA)₂Pb₃I₈·2DMSO before and (b) perovskite after annealing; FAPbI₃ with (d) FAPbI₃·DMF and 2H FAPbI₃ before and (e) perovskite and PbI₂ after annealing. Integrated scattering intensities of Bragg reflections from the structures during the crystallization process of MAPbI₃ and FAPbI₃ compositions. Dashed vertical lines indicate: 1 - beginning of the annealing experiment, (c) MAPbI₃, 2 - end of (MA)₂Pb₃I₈·2DMSO intermediate phase conversion, blue region shows its duration; (f) FAPbI₃, 2 - end of FAPbI₃·DMF intermediate phase conversion, pink region shows its duration, 3 - target temperature increased.

place at $\approx 55^\circ\text{C}$ [126]. The MAPbI₃ crystallites, tracked during the annealing treatment, consisted of a cubic perovskite phase, but were found in the tetragonal phase at room temperature [233]. This composition was previously studied using X-ray diffraction before and after annealing, the DMSO-based intermediate phase was also identified [131]. Nevertheless, the crystal transformation of the intermediate phase was not tracked. In the current study we demonstrate that the optimal annealing conditions, leading to the highest photovoltaic efficiency [229], originate from completing DMSO-based intermediate phase conversion and avoiding the formation of the detrimental PbI₂ phase.

5.2.4. Formamidinium lead iodide

The FAPbI₃ composition was studied to obtain differences in kinetics due to the A-site cation, which leads to higher stability under thermal operation conditions [234] and a bandgap, closer to an 'ideal' single junction solar cell [99]. FAPbI₃ was found to crystallize *via* a sequential process involving several intermediate phases, such as solvent complexes

and the FAPbI_3 δ -phase. Directly after deposition, a DMF-based precursor phase and the 2H FAPbI_3 hexagonal polymorph, co-existing throughout the whole film, were identified (Fig. 5.4(d) and (Fig. B.1)). The precursor phase was characterized by the reflection at $|q| = 0.545 \text{ \AA}^{-1}$, which is presumably a $\text{FAPbI}_3 \cdot \text{DMF}$ phase, similar to the $\text{FAPbI}_3 \cdot 2\text{DMF}$ intermediate phase with one DMF molecule evaporated from the unit cell [147]. This assumption is based on the ability of $\text{FAPbI}_3 \cdot 2\text{DMF}$ to lose one DMF molecule upon drying, which may occur more rapidly at the thin film scale than in solution in a glass vial, to form a stable $\text{FAPbI}_3 \cdot \text{DMF}$ reagent [148], similar to $\text{MAPbI}_3 \cdot \text{DMF}$ [98].

In situ GIWAXS revealed solvent evaporation within the first 30 s, resulting in Bragg intensity increase, followed by a rapid conversion of the DMF-based intermediate phase (~ 110 s, Tab. 5.3) into the 2H FAPbI_3 phase (1 $\rightarrow$ 2 in Fig. 5.4(f)). Directly afterwards, a slow formation of the cubic perovskite phase (2 $\rightarrow$ 3) from the 2H phase, and a more rapid conversion at elevated temperature (3) after 400 s of the annealing scan was identified. The raw *in situ* GIWAXS data during thermal annealing with marked structures is displayed in Fig. B.3(b). The observed intermediate phase showed much faster decomposition in comparison to the DMSO-based phase in MAPbI_3 , which suggests a different microscopic conversion mechanism or lower stability of the DMF intermediate, originating from the differences in properties of the solvents. The intercalated DMF evaporated from the $\text{FAPbI}_3 \cdot \text{DMF}$ phase under annealing and the residual rapidly recrystallized into the 2H FAPbI_3 phase. A comparison of the unit cells, corresponding to the $\text{FAPbI}_3 \cdot 2\text{DMF}$ and 2H FAPbI_3 phases, is displayed in Fig. 5.5.

The final film, displayed in Fig. 5.4(e), consisted of the FAPbI_3 cubic perovskite phase and PbI_2 . Since the annealing conditions of the FAPbI_3 composition were not optimized, a significant amount of PbI_2 was formed (27%, Fig. 5.9) due to the excessive annealing [159, 235, 236]. Previously, it was shown that the FAPbI_3 composition, dissolved in DMF, forms the $\text{FAPbI}_3 \cdot 2\text{DMF}$ intermediate phase [147] with a structural motif of face-connected PbI_6 octahedra, as presented in Fig. 5.5(a). Nevertheless, the precise crystallization kinetics of this composition, deposited as thin film, was not resolved yet. We suggest that the $\text{FAPbI}_3 \cdot 2\text{DMF}$ intermediate phase is metastable within the deposited film and tends to evaporate one of two intercalated DMF molecules, leading to a more stable $\text{FAPbI}_3 \cdot \text{DMF}$ reagent. In order to reveal the complexity of DMF-based intermediate phases in this composition, an additional research was carried out during the complete thin film deposition in the designed spin-coating chamber, more details are presented in Sec. 5.4.

5.2.5. Methylammonium lead bromide

Another perovskite composition which, similarly to MAPbI_3 , was discovered as a visible-light sensitizer, is methylammonium lead bromide (MAPbBr_3) [123]. For preparation, MABr and PbBr_2 were dissolved in DMF as a moderately coordinating solvent for this system [237] and spin-coated onto a glass/FTO/ TiO_2 substrate (Tab. 5.2). Already during spin-coating, MAPbBr_3 adopted a cubic structure [238] at room temperature with the

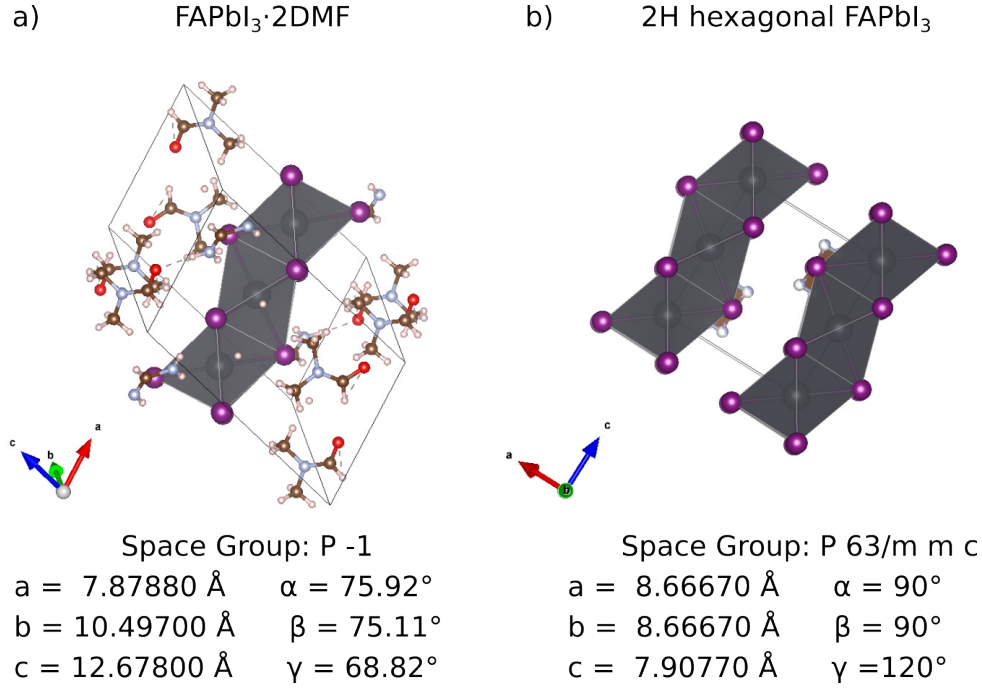


Figure 5.5.: Crystal structure of formamidinium-based phases with unit cell parameters: (a) $\text{FAPbI}_3 \cdot 2\text{DMF}$ [147] and (b) 2H hexagonal FAPbI_3 [71]. In FAPbI_3 and FA:MA compositions, DMF-based intermediate phases convert into the 2H hexagonal pure FAPbI_3 or mixed phase, respectively.

Table 5.3.: Estimated conversion times of the intermediate phases observed in samples with different compositions.

Sample	τ for DMF-based intermediate	τ for $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$
MAPbI_3	—	350 s
FAPbI_3	110 s	—
FA:MA	45 s	250 s
FA:MA:Cs	—	350 s

(100) scattering reflection at $1.062 \text{ \AA}^{-1}$ (Fig. 5.6(a)). The annealing procedure activated the growth of additional perovskite phase crystallites, manifesting in an increase of the scattering signal from the cubic MAPbBr_3 phase, displayed in Fig. 5.6(c). The raw *in situ* GIWAXS data during thermal annealing with marked structures is displayed in Fig. B.4(a).

A comparison of the (100) MAPbBr_3 cubic perovskite GIWAXS reflection before and after annealing is displayed in Fig. 5.7. The perovskite reflection showed a peak shift toward smaller $|q|$ values, indicating an increase of the unit cell parameter of the perovskite phase as a result of heat-assisted crystallization. The FWHM of the perovskite peaks decreased, which suggests an increase of the size of coherently scattering domains, which in combination with the increasing lattice constant indicates the recrystallization process upon heat treatment. An estimation for MAPbBr_3 island size before annealing based on GIWAXS measurements is 40 nm, while after annealing it increased up to 80 nm.

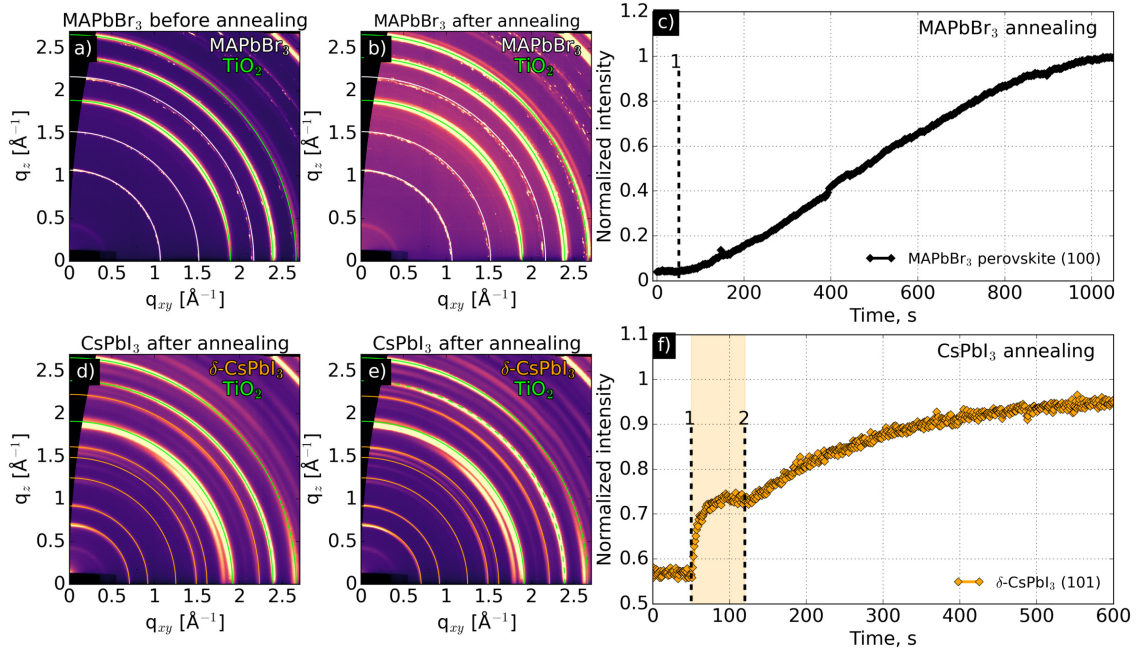


Figure 5.6.: GIWAXS of MAPbBr₃ and CsPbI₃ compositions at 0.2° angle of incidence with marked structures: MAPbBr₃ perovskite (a) before and (b) after annealing; CsPbI₃ with δ -CsPbI₃ (d) before and (e) after annealing. Integrated scattering intensities of Bragg reflections from the structures during crystallization of MAPbBr₃ and CsPbI₃. Dashed vertical lines indicate: 1 - beginning of the annealing experiment, (c) MAPbBr₃, (f) CsPbI₃, 2 - end of the first crystallization step, orange region shows its duration.

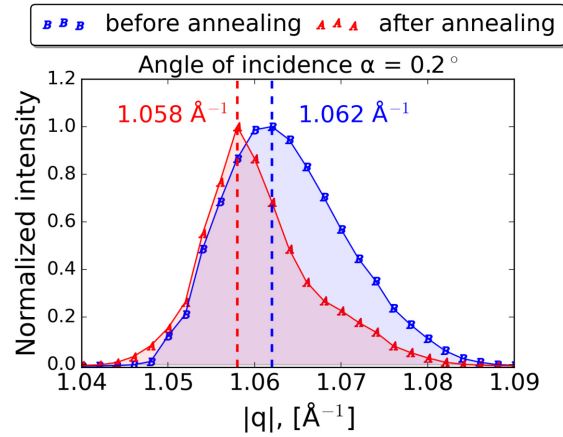


Figure 5.7.: Azimuthally integrated (100) MAPbBr₃ ring intensity of GIWAXS data at 0.2° angle of incidence corresponding to the scattering from the sample bulk before and after annealing treatment. The shift in the Bragg peak maximum corresponds to an increase in the cubic lattice constant, a decrease in the FWHM corresponds to an increase in the scattering island size.

No additional structures were observed by GIWAXS experiments (Fig. 5.6(b)), however, a GIXD scan, displayed in Fig. B.2, indicated the presence of small amounts of PbBr_2 within the final film [239], which could have appeared due to the X-ray damage. We demonstrate the formation of small crystallites of the cubic perovskite phase directly after spin-coating of the MAPbBr_3 composition, while the annealing procedure activated their size growth. The formation of the perovskite phase prior to annealing is typical for bromide-rich phases [39], unlike for iodide-based compositions, which require annealing to initiate the conversion of intermediate phases into the perovskite phase. This is one of the major differences between halides in perovskite composition, which might hint at the origin of halide segregation under light illumination [39].

5.2.6. Cesium lead iodide

To uncover the crystallization pathway of a Cs-based structure, the growth kinetics of the CsPbI_3 composition was studied. It formed a single phase of $\delta\text{-CsPbI}_3$ which showed two-step crystallization kinetics. Directly after spin-coating, the presence of the orthorhombic $\delta\text{-CsPbI}_3$ phase was identified [156, 240], characterized by the reflection at $|q| = 0.7 \text{ \AA}^{-1}$ (Fig. 5.6(d)). Once the annealing started, the $\delta\text{-CsPbI}_3$ Bragg peak intensity showed a rapid increase (1 $\rightarrow$ 2 in Fig. 5.6(f)) lasting 70 s, followed by slower scattering intensity growth. The presence of a rapid increase in intensity may indicate a strong interaction of Cs^+ with lead halide species in the precursor solution [241], which resulted in partial formation of the Cs-based structure within the coated film prior to annealing. The raw *in situ* GIWAXS data during thermal annealing with marked structures is displayed in Fig. B.4(b). A similar trend was observed for other Cs-based phases within the Cs-containing compositions, probed under $\alpha_i = 0.14^\circ$. The annealing procedure was not sufficient for orthorhombic-to-cubic conversion of CsPbI_3 , since the required conversion temperature for this inorganic composition is $\sim 330^\circ\text{C}$ [242] which could not be reached during the experiment.

5.2.7. Summary on single cation compositions

Directly after spin-coating of the MAPbI_3 and FAPbI_3 compositions, different intermediate phases were identified: solvent complexes based on DMSO, namely $((\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO})$ [152]) and on DMF, presumably $(\text{FAPbI}_3 \cdot \text{DMF})$ [147]). Dissimilar conversion speeds reflected their relative stability upon annealing and microscopic differences due to the solvents they were based on. MAPbBr_3 did not form any solvent complexes, but showed the presence of the cubic perovskite phase directly after spin-coating, during annealing the coherently scattering domain size increased. For CsPbI_3 , the annealing temperature was not sufficient for the orthorhombic-to-cubic conversion. Nevertheless, the crystallization kinetics of $\delta\text{-CsPbI}_3$, featuring a two-step intensity increase during annealing, is of great interest for understanding the microscopical behavior of Cs^+ cations within the coated

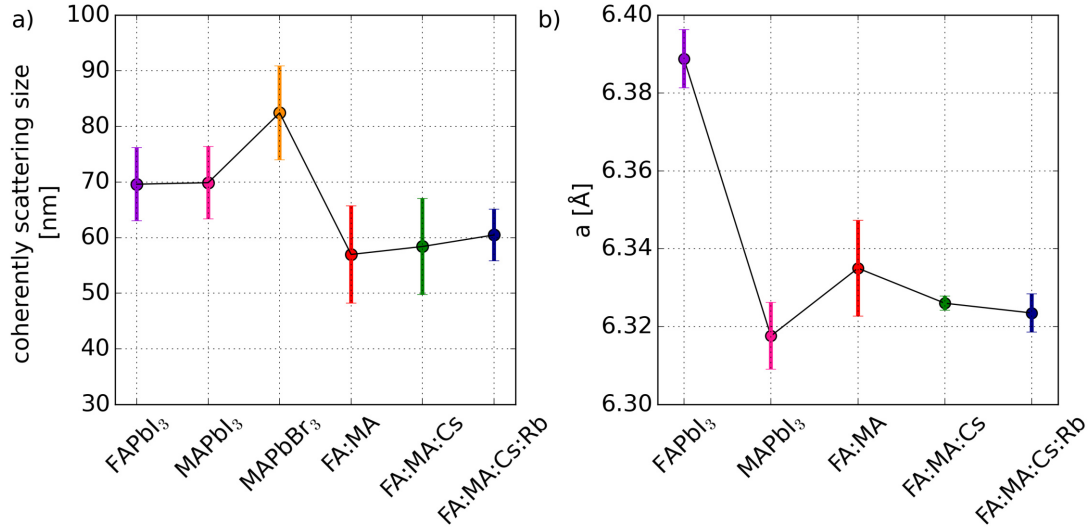


Figure 5.8.: (a) Minimum coherently scattering island size determined from peak widths (FWHM) of GIXD data [243]. Averaging was performed over different crystallographic directions, as similar trends could be observed for all of them. (b) Unit cell parameters, determined from Gaussian fits of peak positions observed in the GIXD data.

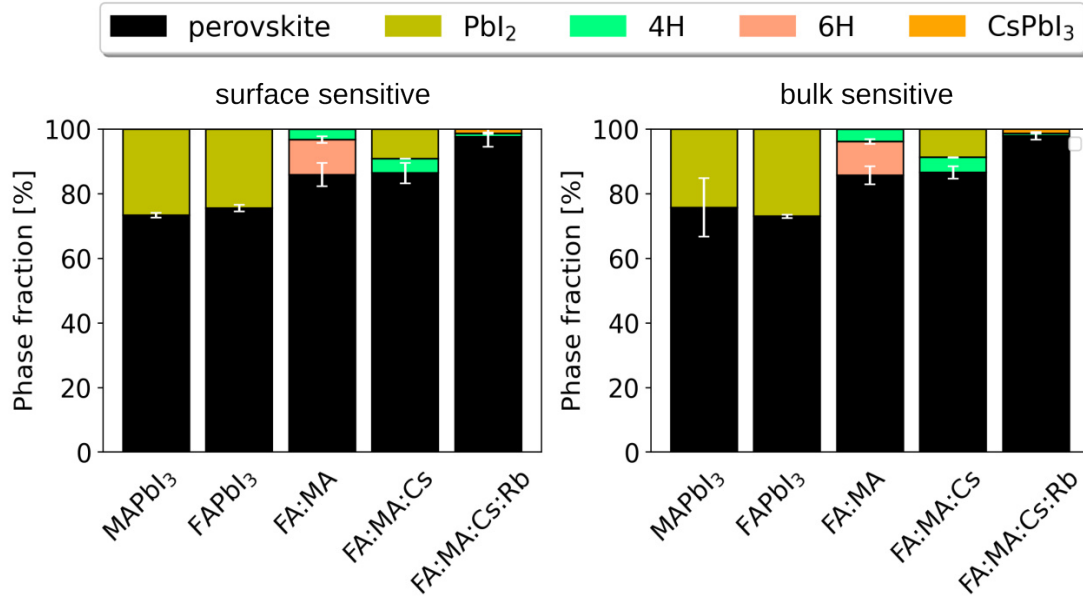


Figure 5.9.: Molar phase fractions of cubic, hexagonal, PbI₂ and δ -CsPbI₃ phases depending on the film composition, determined from peak integration of radial intensity profiles extracted from reciprocal space maps at incidence angles of 0.1° (left, surface-sensitive) and 0.2° (right, bulk-sensitive). Error bars were estimated due to compositional uncertainties and experimental statistics.

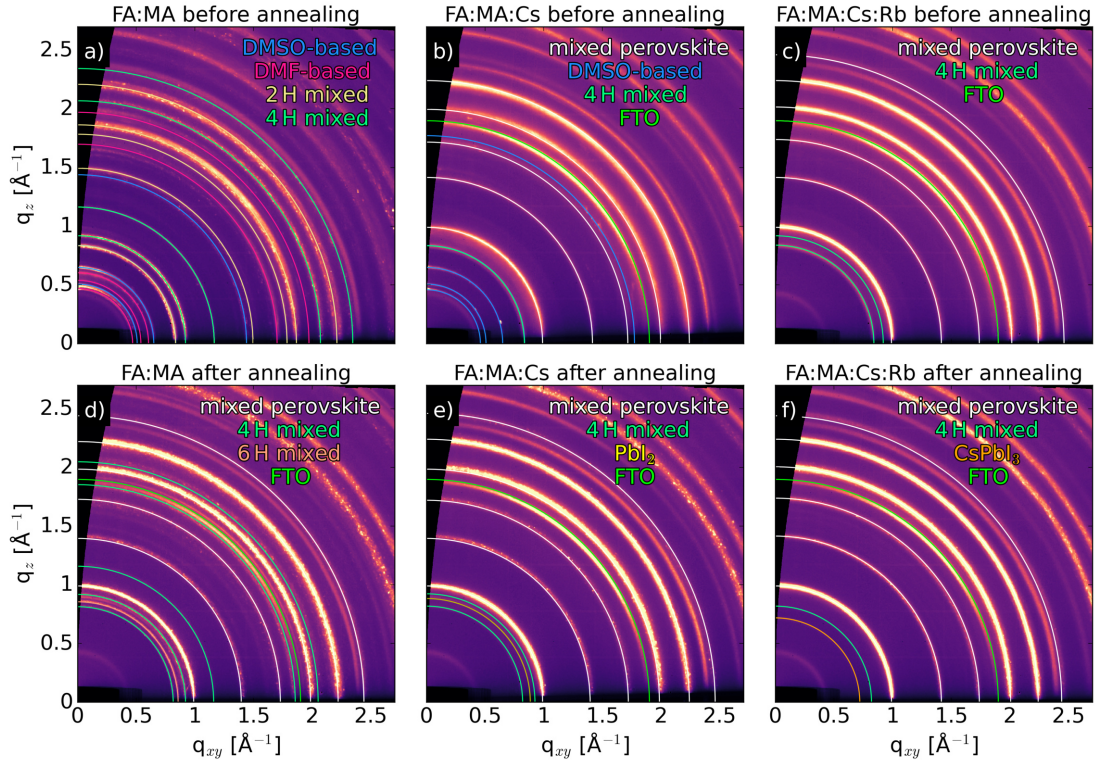


Figure 5.10.: GIWAXS reciprocal space maps of mixed compositions with 0.2° angle of incidence showing structures within the sample bulk before (top row) and after (bottom row) annealing.

thin film also, and especially in the mixed cation compositions discussed below.

5.2.8. Multi-cation samples

Since mixed perovskite compositions are a well-known method to overcome some of the drawbacks of single cation perovskite materials, their crystallization process has been investigated in detail and will be presented and compared in the following sections. The double cation composition $(\text{FAPbI}_3)_{0.83}(\text{MAPbBr}_3)_{0.17}$, denoted FA:MA, was chosen due to its good stability and successful application in single and tandem solar cells [244]. Other compositions were prepared by addition of one or two inorganic iodide salts to the FA:MA composition, resulting in triple or quadruple cation compositions. The precise compositions are the following: $((\text{FAPbI}_3)_{0.83}(\text{MAPbBr}_3)_{0.17})_{0.95}(\text{CsI})_{0.05}$, also denoted as FA:MA:Cs and $((\text{FAPbI}_3)_{0.83}(\text{MAPbBr}_3)_{0.17})_{0.90}(\text{RbI})_{0.05}(\text{CsI})_{0.05}$ referred to as FA:MA:Cs:Rb.

5.2.9. Double cation sample FA:MA

FA:MA composition was previously investigated during OSC [71] and using the antisolvent method [116, 227]. It displayed a complicated crystallization process involving three (2H,

4H and 6H) hexagonal polytypes [71] together with two different solvent-based intermediates. In the current study, the double cation composition had both DMF- and DMSO-based intermediate phases before annealing (Fig. 5.10(a)). The DMSO-based intermediate was $(\text{MA})_3\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ [152], the same as in the studied MAPbI_3 composition. The identified DMF-based intermediate phase showed three intense reflections located at $0.48 \text{ \AA}^{-1}$ (020), $0.525 \text{ \AA}^{-1}$ (001) and $0.585 \text{ \AA}^{-1}$ (011), which slightly differ from the MAPbI_3 -DMF structure [98]. We propose that the observed phase consists of a combination of MAI, FAI, PbI_2 and $x\text{-DMF}$ and appears in the deposited film during the delay between the spin-coating and annealing procedures as a preliminary state of the 2H hexagonal phase with intercalated DMF molecules. A mixture of the 2H and 4H hexagonal polymorphs [71] was located between the solvent complex phases, which, based on the GIWAXS before annealing, displayed in Fig. B.1, were found closer to the surface (DMF-based) or to the substrate (DMSO-based).

The raw *in situ* GIWAXS data during thermal annealing with marked structures is displayed in Fig. B.5. The 2H phase scattering intensity increased once the annealing started, its further growth followed the fast conversion of the DMF-based intermediate phase (1→2 marked in Fig. 5.11(a,b)). The latter process can be described as the evaporation of DMF molecules and crystallization in the form of the 2H hexagonal polytype, the crystal structures of $\text{FAPbI}_3 \cdot 2\text{DMF}$ and 2H FAPbI_3 , showing obvious similarities, are displayed in Fig. 5.5. The temporal evolution of the positions of the Bragg peaks corresponding to the three observed reflections from the DMF-based phase [98] is shown in Fig. 5.12. The (020) reflection shifts towards higher $|q|$, while (001) and (011) shift towards lower $|q|$: (001) and (011) reflect a decrease in the unit cell parameter b and an increase in the unit cell parameter c , which suggests the evaporation of DMF molecules under annealing treatment from the observed structure and its heterogeneous distribution within the film. The DMSO-based intermediate phase converted into other phases within $\sim 250 \text{ s}$ (1→3 in Fig. 5.11(a,b)), slower than the DMF-based intermediate phase, which is possibly due to the differences in solvent-induced interaction and complexation strength (Tab. 5.3). The 2H hexagonal polytype fully converted into the 4H phase, which showed its scattering intensity maximum after 45 s of annealing, and immediately started to convert to the 6H hexagonal phase. The 6H phase then partially converted to the perovskite phase at the end of the annealing experiment, resembling the 2H-4H-6H perovskite sequence previously demonstrated for a comparable composition deposited by antisolvent-assisted deposition [71, 116]. The rapid increase in scattering intensity observed for the 4H hexagonal polytype can be attributed to the lower formation energy for the 4H FAPbBr_3 phase, as calculated by DFT [227].

After annealing, the presence of perovskite phase as well as 6H and 4H hexagonal polymorphs was observed within the film, as presented in Fig. 5.10(d). Perovskite and 6H hexagonal phases co-existed on top of the resulting thin film, whereas the 4H hexagonal phase was found closer to the substrate (Fig. B.1). This can be explained by combining

the GIWAXS patterns before, during and after annealing, summarized in Fig. 5.11(d): the $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ phase, which was closer to the substrate before annealing, combined with the DMF-based intermediate, found closer to the surface, and converted into the 4H mixed phase. Based on the crystallization sequence of the FA:MA composition, 6H hexagonal phase was formed on top of the existing 4H hexagonal phase layer, which then converted into the mixed perovskite phase closer to the film surface. GIXD of the final film (Fig. 5.11(e)) showed a tiny amount of PbI_2 presumably due to the annealing-induced damage. A complete crystallization sequence of the FA:MA composition was revealed during the one-step deposition method, reflecting the natural processes occurring only due to the annealing treatment.

5.2.10. Triple cation sample FA:MA:Cs

The addition of 5% Cs^+ as a third cation into the FA:MA composition leads to a thermally stable perovskite phase with less impurities and reduced sensitivity to processing conditions [245]. Adding Cs^+ inorganic cation was found to prevent the formation of DMF-based, 2H and 6H phases in the crystallization sequence, which led to perovskite phase formation before annealing and its higher content in the final film. The GIWAXS data after spin-coating of the FA:MA:Cs composition, displayed in Fig. 5.10(b), suggested the presence of $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ solvent complex [152], 4H mixed polytype [71] and mixed perovskite phase. Similarly to the FA:MA composition, the DMSO-based intermediate phase was found closer to the substrate (Fig. B.1), while solvent-free phases crystallized closer to the surface possibly due to the solvent evaporation. From the 4H hexagonal phase for the triple cation composition only (100) reflection could be detected, in contrast to (100) and (101) in the FA:MA composition, which may indicate a lower crystallinity/amount of 4H phase, which therefore suggests a stabilization of the perovskite phase when the number of cations is increased.

The raw *in situ* GIWAXS data during thermal annealing with marked structures is displayed in Fig. B.7(a). Time dependent Bragg peak intensities during annealing of the FA:MA:Cs composition show that the perovskite phase crystallized in two steps, the first step indicated by 1→2 in Fig. 5.13(a). The sample showed the presence of a partially crystallized perovskite phase, similar to the preliminary crystallization of the Cs-containing orthorhombic phase, found in the CsPbI_3 sample, displayed in Fig. 5.6(f). This suggests the presence of predominant organization of the framework precursor by Cs^+ cation that eventually converts into the target perovskite phase [241]. It is followed by a slower intensity increase due to the conversion of the DMSO-based intermediate phase and the 4H hexagonal phase into the mixed perovskite phase. Similarly to the FA:MA composition, the 4H hexagonal served as an intermediate step in the crystallization process, its Bragg peak intensity increased, indicating its important role in the transformation process. This again coincides with the DFT calculation suggesting the lower formation energy for the 4H FAPbBr_3 phase [227]. The conversion rate of the DMSO-based intermediate was similar

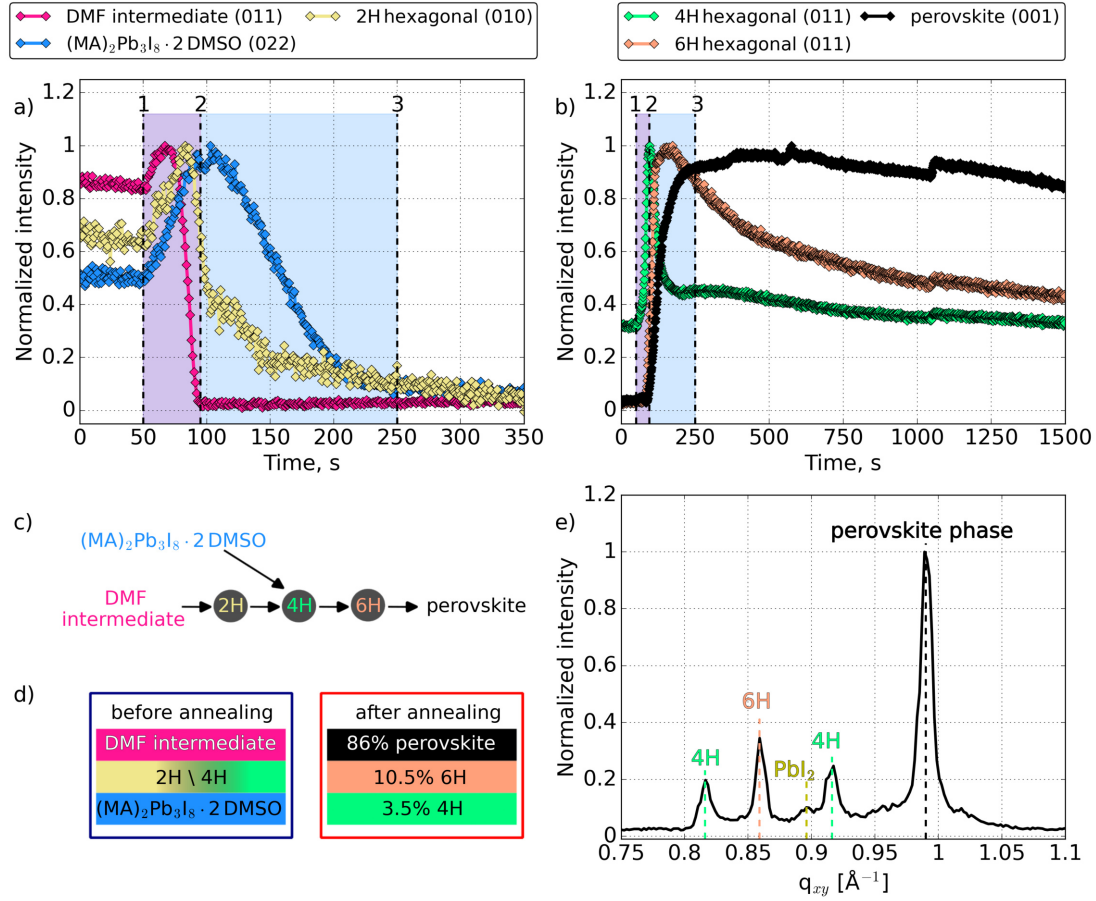


Figure 5.11.: Sample FA:MA: integrated intensities of the structures during sample annealing: (a) $\text{FAPbI}_3 \cdot \text{DMF}$, $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ and 2H mixed hexagonal phase; (b) cubic perovskite, 4H and 6H hexagonal phases. 1 - beginning of the annealing experiment; 2 - end of $\text{FAPbI}_3 \cdot \text{DMF}$ intermediate phase conversion, pink region shows its duration; 3 - end of Pb_3I_8 intermediate phase conversion, blue region shows its duration. (c) Sketch illustrating the conversion behavior during FA:MA sample annealing. (d) Illustration of the layout within the sample before and after annealing. (e) Postgrowth GIXD scan of FA:MA sample revealing the co-existence of cubic perovskite, PbI_2 , 4H and 6H hexagonal phases.

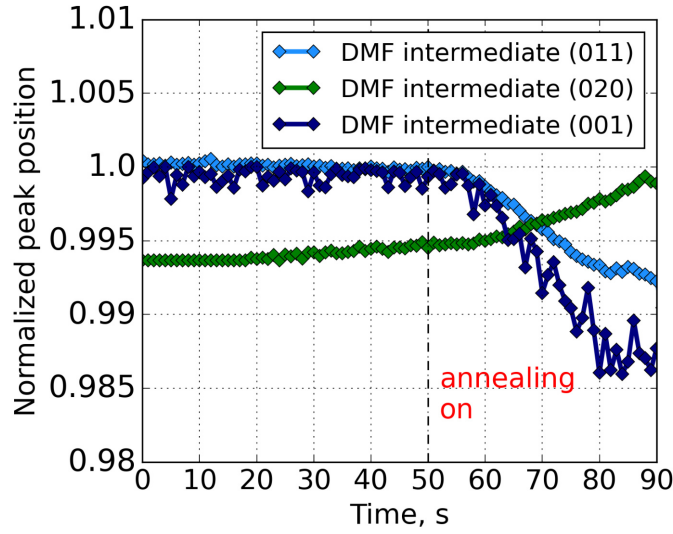


Figure 5.12.: Normalized Bragg peak positions from DMF-based solvent complex in FA:MA composition estimated from Gaussian fit of in situ GIWAXS data, displayed in Fig. B.5. Scattering signals from planes (011) and (001) shift towards lower $|q|$ values upon annealing, indicating c lattice constant increase, while (020) reflection shifts towards higher $|q|$ values, indicating b lattice constant decrease.

to the single cation sample and slower than in the FA:MA sample (Tab. 5.3). A slow conversion to PbI_2 was observed as a result of thermally-induced perovskite degradation [246], which can be avoided by the adjustment of the annealing parameters.

The GIWAXS data after annealing, and the analysis, presented in Fig. 5.10(e) and Fig. B.1, respectively, exhibit scattering features from the 4H hexagonal phase, mixed perovskite phase and a minor amount of PbI_2 , the latter phase is located closer to the substrate. The incorporation of 5% of CsI prevented the formation of 2H and 6H hexagonal phases in the conversion sequence which resulted in perovskite phase stabilization. This observation is in agreement with the previously published research [247], where FA:MA:Cs was tracked by in situ GIWAXS during spin-coating. Nevertheless, we observed an additional iodide- and DMSO-based intermediate phase [152], involved in thin film growth, and might have served as a source of MA and iodide which blended into the mixed perovskite upon annealing. The size of coherently scattering islands and the unit cell parameter are displayed in Fig. 5.8. The unit cell parameter decreased in comparison to the FA:MA sample, indicating a successful incorporation of Cs^+ cations [248, 249], which are smaller than MA^+ and FA^+ cations [137].

5.2.11. Quadruple cation sample FA:MA:Cs:Rb

To further increase the perovskite phase stability we add a second inorganic cation Rb^+ to the FA:MA:Cs composition, and study its crystallization kinetics. The addition of Rb

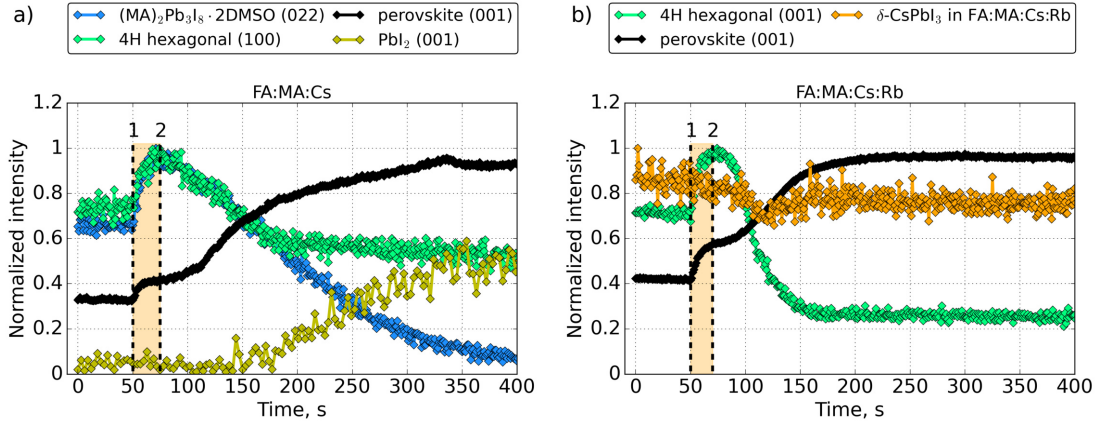


Figure 5.13.: Integrated scattering intensities of the structures during crystallization of mixed cation compositions: (a) FA:MA:Cs and (b) FA:MA:Cs:Rb: 1 - beginning of the annealing experiment, 2 - end of the first crystallization step in the mixed sample, orange region shows its duration.

suppressed the formation of the DMSO-based intermediate phase, resulting in the highest perovskite phase content within the film. The GIWAXS data before annealing, displayed in Fig. 5.10(c), show the presence of two phases: 4H hexagonal polytype [71] and mixed perovskite phase, without any solvent-based intermediate phases. This result hints towards a significant perovskite phase stabilization already prior to annealing, which leads to the more controllable crystallization process.

The raw *in situ* GIWAXS data during thermal annealing with marked structures is displayed in Fig. B.7(b). In addition to the observed phases, some of δ -CsPbI₃ phase [240] with its reflection at $|q| = 0.70 \text{ \AA}^{-1}$, was found within the film during annealing, as presented in Fig. 5.13(b). The annealing treatment induced a rapid increase of the 4H hexagonal phase scattering intensity, similarly to the FA:MA and FA:MA:Cs compositions, indicating an important role of this phase in the crystallization sequence of the FA-dominating mixed cation compositions. The 4H phase mainly converted into the desired mixed perovskite phase. Crystallization of the perovskite phase went faster than in any other composition and showed a two step growth form, similar to CsPbI₃ and FA:MA:Cs (compare Fig. 5.6(f) and Fig. 5.13(a,b)). The Bragg peak intensity of δ -CsPbI₃ in FA:MA:Cs:Rb composition decreases simultaneously with the jump-like perovskite scattering intensity increase (1→2 in Fig. 5.13(b)) during the first step, indicating the preliminary formation of perovskite phase within the deposited film, driven by the high interactivity of Cs⁺ cations [241]. The subsequent increase of the perovskite scattering intensity (2→3 in Fig. 5.13(b)) is due to the partial decomposition of the CsPbI₃ phase, as its scattering intensity increased to a limited extent after 70 s of the annealing treatment. This fact leads to the conclusion that some of the Cs⁺ cations got incorporated into the mixed perovskite phase during the initial stage of the annealing treatment.

The GIWAXS data with varying angles of incidence and its analysis, displayed in

Fig. 5.10(f) and Fig. B.1, suggest that the δ -CsPbI₃ phase is located on the bottom of the sample closer to the substrate and indicates incomplete incorporation of cesium into the mixed perovskite phase, which is similar to the previous research on other mixed cation compositions [51]. Nevertheless, the quasi-cubic unit cell parameter, estimated from GIXD, decreased in comparison to the FA:MA:Cs composition, as displayed in Fig. 5.8. The mixed perovskite phase in the final film is located under the hexagonal 4H phase, similarly to the FA:MA:Cs composition, as presented in Fig. B.1, which reflects some similarities in the crystallization kinetics of compositions with stabilized perovskite phase, which forms prior to annealing. The addition of 5% RbI in the FA:MA:Cs composition led to the highest amount of perovskite phase (97.5%) within the studied thin films (Fig. 5.9). This result is supported by previous studies [138, 141, 245] and establishes the success of mixing cations for perovskite thin film quality and stability.

Crystallization kinetics of Cs-containing compositions

The evolution of scattering intensities from Cs-containing structures were fitted with the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model [250] to describe the behavior of Cs⁺ cations within the Cs-containing phases within the deposited thin films. This assumption was made based on an unusual shape of the scattering intensity from the Cs-containing phases. Another hint towards observing the scattering signal exclusively from Cs-containing phases comes from the critical angle of CsPbI₃ for 22 keV which is $\sim 0.12^\circ$ as displayed in Fig. 2.11, while the angle of incidence α_i for the *in situ* GIWAXS experiment was 0.14° . The diffraction peak intensity depends on different parameters which are not directly related to the amount of a crystalline phase, such as the grain size and shape, orientation and scattering factors [251]. A predicted peak area corresponding to its maximum value (A_{max}) for the first crystallization step can be estimated by fitting the scattering data from Cs-containing phases with the JMAK model [250]. It was used to fit the intensity curves reflecting the formation of orthorhombic (CsPbI₃ composition) or mixed perovskite (within the FA:MA:Cs and FA:MA:Cs:Rb compositions) phases:

$$A = A_{max}(1 - \exp(-k(t - t_0)^n)) + C, \quad (5.1)$$

where A is a peak area, A_{max} is a maximum peak area corresponding to full conversion, t -time, t_0 -the onset of the process (in current experiment $t_0 = 50$ s, the moment when annealing started), k -reaction rate constant, n -reaction order [251]. The reaction rate increased, while the reaction order decreased with decreasing percentage of Cs within the fitted phases (δ -CsPbI₃ < mixed perovskite in FA:MA:Cs < mixed perovskite in FA:MA:Cs:Rb), as it reflects the amount of Cs involved in the formation. The decreasing duration of the first crystallization step can be explained by the reducing amount of Cs⁺ incorporated into the observed structure: for the CsPbI₃ composition δ -CsPbI₃ is the only phase within the film, i.e. 100%, while for the mixed cation samples (FA:MA:Cs and FA:MA:Cs:Rb) CsI

Table 5.4.: List of fitted parameters by the JMAK model for Cs-containing samples, reflecting the first crystallization step

Sample	Phase	A_{max}	k	n	C	Duration in s
CsPbI ₃	orthorhombic	0.4236	0.3709	0.624	0.755	70
FA:MA:Cs	mixed perovskite	0.5081	0.2982	0.84	1.498	25
FA:MA:Cs:Rb	mixed perovskite	1.2166	0.1757	0.918	2.525	20

takes $\sim 5\%$ of the target composition. Since Cs⁺ cations were not fully incorporated into the quadruple cation sample, its duration is lower than that of the mixed perovskite phase in a triple cation composition.

5.2.12. Summary on mixed cation compositions produced by one-step method

This study revealed the crystallization pathways of single and mixed cation perovskite compositions during one-step preparation studied by *in situ* GIWAXS. Single cation compositions show the presence of solvent-based intermediate phases: (MA)₂Pb₃I₈·2DMSO in MAPbI₃ and presumably FAPbI₃·DMF in FAPbI₃. These compositions do not show the presence of perovskite phase prior to annealing, which might be a common feature of the pure iodide-based compositions, deposited by one-step method. During the annealing process, it was observed that the DMF-based intermediate phase undergoes a faster conversion compared to the DMSO-based phase, suggesting a dissimilarity between their respective structures. The MAPbBr₃ composition does not form any solvent complexes, and, in contrast to iodide-based compositions, crystallizes directly as cubic perovskite phase already after spin-coating. The annealing process results in an increase in the size of the coherently scattering islands from 40 nm to 80 nm, and in a slight increase in the unit cell size, which is related to the recrystallization process of the perovskite domains.

After spin-coating, the double cation FA:MA composition has both DMF- and DMSO-based intermediate phases, coexisting with 2H and 4H mixed hexagonal phases. The formation of the DMF-based intermediate within double cation compositions was not reported previously, possibly due to its postponed formation. The crystallization process involves the three hexagonal polytypes: 2H, 4H and 6H phases, with 4H having a remarkable Bragg peak intensity increase, which might be due to its high bromide concentration, and thus a lower formation energy, as it was predicted by the DFT calculations [227]. The final film exhibits 4H and 6H hexagonal phases and a mixed perovskite phase, taking up to $\sim 85\%$ of the molar phase fraction. The incorporation of 5% Cs⁺ or 5% Cs⁺ and 5% Rb⁺ into the FA:MA composition leads to partial perovskite phase formation before the annealing treatment. The mixing of cations and halides suppresses the formation of multiple hexagonal phase polytypes, thus favoring the formation of the perovskite phase. The crystallization procedure for compositions with three and four cations involves only the 4H hexagonal polytype, which appears as an intermediate step between the solvent-based

complexes and the mixed perovskite phase. We demonstrate that the "natural" temporal evolution of the antisolvent-free films differs from the films with prolonged spin-coating times and from the antisolvent-assisted films, since any additional treatment influences the energetics within the supersaturated films. The biggest fraction of the perovskite phase ($\sim 97.6\%$), co-existing with 4H hexagonal polytype and δ -CsPbI₃ (1.2% of each), was achieved in the quadruple cation composition, indicating the beneficial effect of mixing cations on perovskite phase stabilization. The unit cell parameter, estimated from GIXD measurements, decreased with the addition of inorganic cations, indicating their successful incorporation into the mixed perovskite phase. The coherently scattering island sizes increase going from double cation to quadruple cation compositions, which might be beneficial for solar cell application. All Cs-containing phases show similar two-step growth dynamics during the crystallization process, possibly originating from the strong interaction of Cs⁺ with the lead halide species within the precursor solution, which results in forming Cs-based structures, predicted previously [241]. This is further supported by the proximity of the critical angle for the CsPbI₃ structure, which is $\sim 0.12^\circ$, to the angle of incidence during *in situ* GIWAXS experiment, which was 0.14° . Then, the rapid scattering intensity increase might exclusively be caused by Cs⁺.

Present section revealed the complexity of the processes, occurring within the perovskite thin films deposited by one-step method and probed by *in situ* X-ray scattering during hot-plate annealing. However, one of the intermediate phases, namely FAPbI₃·DMF, observed during the FAPbI₃ thin film growth, was identified by only one Bragg peak. Therefore, an additional research on the origins and complexities of FA- and DMF-based intermediate phases was carried out during spin-coating and annealing procedures of the FAPbI₃ composition in the designed chamber, and will be presented in the next sections.

5.3. Experimental details

The following sections within the present chapter are based on the measurements at P08 beamline [181] at PETRA III/DESY, produced in the spin-coating chamber [36], designed in the current work and described in Chap. 4. The major amount of compositions was deposited with default parameters (if not stated otherwise) onto 1 mm thick 10×10 mm bare or ITO-coated glass substrates, by three methods: OSC, antisolvent-assisted deposition and gas quenching-assisted deposition. The sample fabrication procedure was as follows: 40 μ L of perovskite precursor solution was applied onto the argon plasma-cleaned substrate, described in Subsec. 2.3.1, followed by one of the three deposition methods. OSC included spin-coating at 1000 rpm for 10 s and at 4000 rpm for 30 s (Fig. 2.16). Antisolvent-assisted deposition included spin-coating with the same spinning parameters (1000 rpm for 10 s and 4000 rpm for 30 s), 200 μ L of antisolvent was dropped onto the spinning substrate during the second spin-coating step at the 35th second (Fig. 2.18). The gas quenching method included spin-coating at 3000 rpm for 150 s, the nitrogen stream was switched

on 15 s after the start of spinning for 135 s (both of them, spinning and gas quenching, stopped simultaneously), and induced the supersaturation of the deposited film, followed by rapid crystallization, as described in Subsec. 2.3.5.

The annealing was done by the NIR halogen lamp with a golden reflector, which was described in Subsec. 4.2.4, typically at the power of 150 W in order to initiate solvent evaporation and approach target temperature, followed by the annealing at 85 W to finalize the crystallization process. For all samples, discussed in the following sections, lamp-to-sample distance was chosen to be 40 mm, which corresponds to the highest efficiency of the NIR-based annealing. This geometry was found to be optimal for the synchrotron-based experiments. *In situ* GIWAXS patterns were generated by 18 keV X-rays ($\lambda = 0.69 \text{ \AA}$) with a beam size of $500 \mu\text{m}$ (horizontal) $\times$ $100 \mu\text{m}$ (vertical) at an angle of incidence of 0.5° at 0.1 s intervals by a 2D PerkinElmer detector (XRD 1621 CN3 EHS, 2048×2048 pixel) located at a distance $L = 809 \text{ mm}$ from the sample.

5.4. Additional research on FA- and DMF-based intermediate phases

A follow up research on the origins of the DMF-based intermediate [147], presumably $\text{FAPbI}_3 \cdot \text{DMF}$, observed in Subsec. 5.2.4, was conducted. In order to extend the structural analysis and reproduce growth conditions, FAPbI_3 composition was dissolved in pure DMF solvent and deposited onto the ITO-coated glass substrates at reduced nitrogen stream (less inert atmosphere), which is similar to the default annealing procedure under the kapton dome for previously discussed samples. In order to extend an understanding of FAPbI_3 composition growth kinetics, it was deposited using various methods: OSC, ethanol antisolvent-assisted spin-coating, and spin-coating with simultaneous spinning/gas quenching/heating treatment. The information obtained is aimed at gaining additional knowledge on the role of the DMF solvent molecules in the precursor solution and its ability to form solvent-based intermediate phases within the deposited film before and during the annealing treatment.

5.4.1. Formamidinium lead iodide during one-step deposition

The crystallization of FAPbI_3 during one-step spin-coating deposition and annealing treatment tracked by GIWAXS is displayed in Fig. 5.14. During the second spin-coating step at 4000 rpm, the formation of the following structures was identified: $(\text{FA})_2\text{Pb}_3\text{I}_8 \cdot 4\text{DMF}$ [147] with its reflections at $0.63 \text{ \AA}^{-1}$ and $1.02 \text{ \AA}^{-1}$, $\text{FAPbI}_3 \cdot 2\text{DMF}$ [147] with its reflections at $0.52 \text{ \AA}^{-1}$, $0.75 \text{ \AA}^{-1}$ and $0.895 \text{ \AA}^{-1}$, presumably $\text{FAPbI}_3 \cdot \text{DMF}$ with its reflection at $0.56 \text{ \AA}^{-1}$ (previously observed in Fig. 5.4(f)) and 2H FAPbI_3 hexagonal phase [71] with its reflections at $0.83 \text{ \AA}^{-1}$ and $1.15 \text{ \AA}^{-1}$. The scattering signals from the first two structures approached their maxima $\sim 25 \text{ s}$ after the end of spinning, and partially converted into the latter

two phases: $\text{FAPbI}_3 \cdot \text{DMF}$ (slow growth) and 2H FAPbI_3 (rapid growth), as displayed in Fig. 5.14(d). This might originate from the behavior of the intercalated DMF molecules: 4DMF- and 2DMF-based intermediate phases are not stable within the deposited film, while $\text{FAPbI}_3 \cdot \text{DMF}$ is formed as a metastable phase and transforms into the 2H FAPbI_3 due to the similarities in their crystal structure, displayed in Fig. 5.5.

Due to the relatively high volatility of DMF, in comparison to DMSO [94], the 4DMF-

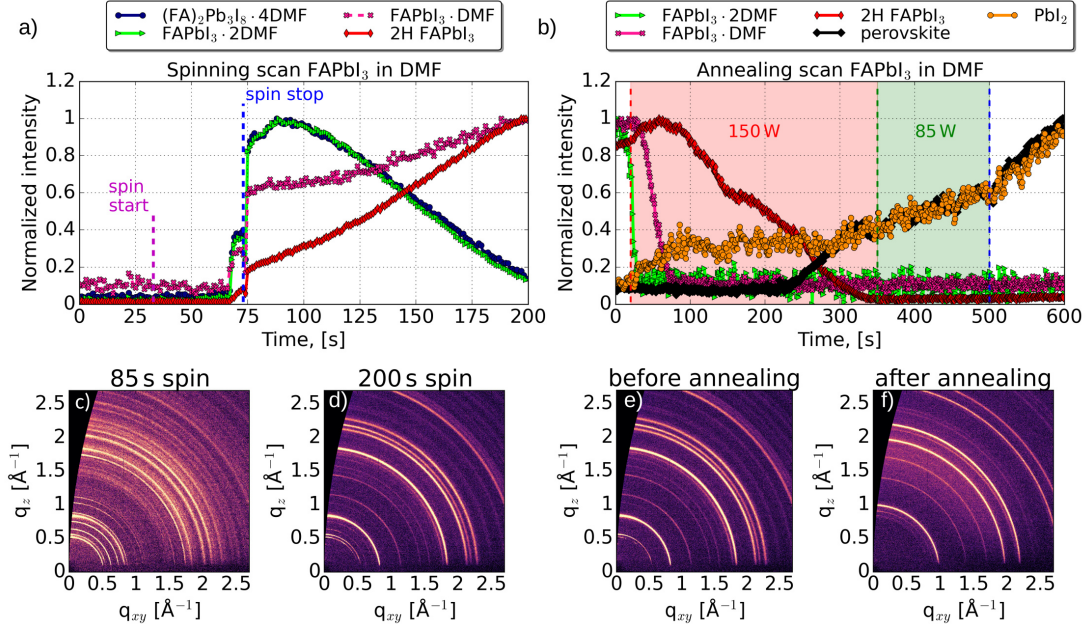


Figure 5.14.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) spin-coating and (b) annealing steps of FAPbI_3 composition dissolved in DMF and deposited by OSC method. Annealing was done for 330 s at 150 W and 150 s at 85 W. Exemplary GIWAXS scans during (c), (d) spinning scan, (e) before and (f) after annealing.

based intermediate phase was no longer observed before annealing, unlike the 2DMF-based intermediate phase which is more stable. The annealing treatment initiated an immediate conversion of $\text{FAPbI}_3 \cdot 2\text{DMF}$ into the $\text{FAPbI}_3 \cdot \text{DMF}$ and 2H hexagonal FAPbI_3 phases, while $\text{FAPbI}_3 \cdot \text{DMF}$ solvent complex converted into the hexagonal phase slower, within 80 s, similarly to 110 s when the same composition was annealed on a hotplate, compare Fig. 5.14(b) and Tab. 5.3. The DMF-based intermediate phase decomposition led to hexagonal phase scattering intensity increase, followed by slow conversion into the cubic FAPbI_3 perovskite phase. The scattering intensity of the latter phase started to rise after 200 s of the annealing treatment at 150 W. The major part of the hexagonal-to-cubic conversion took place within 120 s, followed by a slow increase of perovskite phase scattering intensity until the end of the annealing scan. Additionally, a tiny amount of PbI_2 with its Bragg peak at $|q| = 0.89 \text{ \AA}^{-1}$ was formed [228], mainly when the conversion was over, as a result of partial material decomposition, which can be seen in Fig. 5.14(f). The

final sample looked similar to the previously analysed FAPbI₃ composition spin-coated onto FTO-coated glass substrate (compare Fig. 5.14(f) and Fig. 5.4(e)). The additional measurement allowed to extend the knowledge regarding the intermediate phases, formed after spin-coating. The precursor solution forms DMF-based intermediate phases with one, two and four intercalated DMF molecules, due to their non-volatile nature [94]. The phases with two or four DMF molecules converted into the FAPbI₃·DMF intermediate phase, being a metastable state of the deposited material, which then converted into the 2H FAPbI₃ hexagonal phase during solvent evaporation. The conversion upon annealing complete the conversion of the solvent-based intermediate phase into hexagonal phase, which then converted into the perovskite phase, in the same manner as it was observed in Subsec. 5.2.4. This result proves the existence of the FAPbI₃·DMF phase, in contrast to the previously published research, which claimed that, unlike MA⁺, FA⁺ is not able to form a structure with only one DMF molecule [147]

5.4.2. Formamidinium lead iodide during ethanol antisolvent-assisted spin-coating

The crystallization of FAPbI₃ during ethanol antisolvent-assisted spin-coating deposition and annealing treatment tracked by *in situ* GIWAXS is displayed in Fig. 5.15. Antisolvent application initiated rapid crystallization by removing the excess of DMF solvent, resulting in an immediate formation of the 2H FAPbI₃ hexagonal phase, characterized by its reflection at 0.83 Å⁻¹, as displayed in Fig. 5.15(a). The DMF-intermediate phases, namely FAPbI₃·4DMF, FAPbI₃·2DMF and FAPbI₃·DMF [147], rapidly formed with a short delay (~2.5 s) after antisolvent application, their scattering intensity maxima were reached once the spinning was over. The formed intermediate phases partially converted into the 2H hexagonal phase [71] (compare Fig. 5.15(c) and Fig. 5.15(d)). It might indicate a saturation within the coated film and rapid solidification due to the critical removal of the excess solvent by an antisolvent, while in the case of one-step deposition FAPbI₃·DMF phase formed from the DMF-rich intermediate phases and was metastable, as it was shown in Subsec. 5.4.1. Similarly to one-step method, annealing procedure initiated the conversion of the FAPbI₃·DMF phase into the 2H hexagonal phase (Fig. 5.15(b)). Due to the much smaller content of this solvent-based intermediate phase, the conversion went much faster, and it was over after ~10 s of annealing (80 s for one-step method). The scattering intensity from cubic perovskite phase started to increase after 30 s of annealing at 150 W (200 s in OSC method), the hexagonal-to-cubic conversion was over within ~100 s (120 s in OSC method). Further annealing led to the formation of PbI₂ within the final film, characterized by the scattering reflection at 0.9 Å⁻¹, as a result of partial decomposition [228], which can be observed in Fig. 5.15(f). The final sample had a better coverage than the one deposited by one-step method, as it is a positive effect of antisolvent application, compare Fig. 5.15(f) and Fig. 5.14(f). The ethanol antisolvent application changed the crystal-

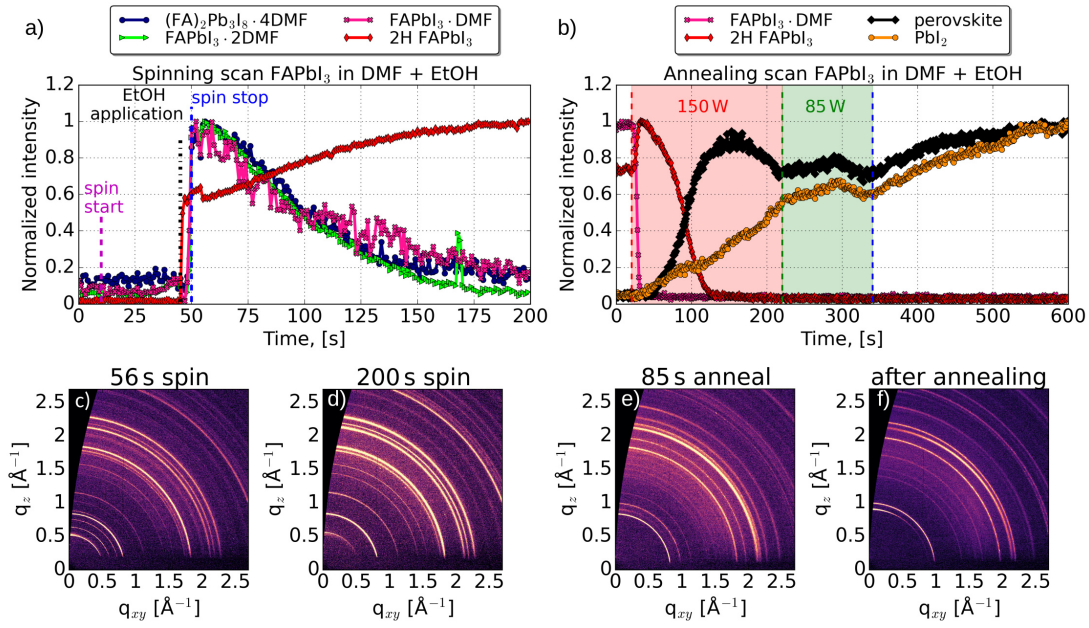


Figure 5.15.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) ethanol antisolvent-assisted spin-coating and (b) annealing steps of FAPbI₃ perovskite (dissolved in DMF, deposited on ITO-coated glass substrate) thin film fabrication. Annealing was done for 200 s at 150 W and 120 s at 85 W. Exemplary GIWAXS scans (c), (d) after ethanol application; (e) during and (f) after annealing - perovskite thin film with a tiny fraction of PbI₂.

lization kinetics due to the rapid solvent extraction: FAPbI₃·DMF phase was no longer metastable, it converted into the 2H hexagonal FAPbI₃ phase even before the annealing treatment.

5.4.3. Simultaneous spinning/gas quenching/annealing of FAPbI₃ composition.

The FAPbI₃ composition dissolved in DMF was deposited by a combination of methods, including simultaneous spinning, annealing and nitrogen flow application. The scattering intensity oscillations of all phases, displayed in Fig. 5.16(b), originate either from the overlap of the spinning frequency, which was 3000 rpm (50 rps) and 300 rpm (5 rps), and *in situ* GIWAXS sampling frequency, which was 10 images/second, or from the sample rotation while the chamber was moved by the *xy* stage, and the incoming X-rays were not focused on the center of rotation. Precursor solution was deposited onto the ITO-coated glass substrate, the annealing treatment with lamp power at 90 W started at 50 s of the scan and lasted for ~430 s, the halogen lamp almost immediately partially evaporated the DMF solvent, and induced the appearance of the reflections at 0.83 Å⁻¹ and 1.15 Å⁻¹, corresponding to the 2H hexagonal FAPbI₃ phase [71]. On the other side, once N₂ stream

Table 5.5.: Structural composition of the studied samples and solvents.

Sample	Solvent	Substrate
MAPbBr ₃	DMF:DMSO (4:1)	Glass
FAPbI ₃	DMF:DMSO (4:1)	Glass
MAPbI ₃	DMF:DMSO (4:1)	Glass
FA:MA	DMF:DMSO (4:1)	Glass
FA:MA:Cs	DMF:DMSO (4:1)	Glass

was switched on, the scattering intensity of hexagonal phase slightly decreased, while the scattering intensity from 2DMF- and 4DMF-based intermediate phases showed a rapid increase. This is a remarkable result from using a combination of heating and gas quenching: the formation of the FAPbI₃-DMF intermediate phase was suppressed within the film. The spinning of the sample at 3000 rpm distributed the solution and, combined with a nitrogen flow treatment, initiated a further increase of the scattering intensities from the intermediate phases, which lasted for ~ 100 s of spinning, while hexagonal phase scattering intensity oscillated around a constant value. Then, both intermediate phases almost fully converted into the 2H hexagonal phase within 20 s. This might be a direct influence of annealing, which evaporated a substantial amount of DMF molecules. The major fraction of the 2H hexagonal phase ($\sim 90\%$) converted into perovskite cubic phase within 50 s of annealing at 90 W, which is at least 2 times faster than for the previous two methods (120 s for OSC method and ~ 100 s for antisolvent-assisted method). After conversion, a tiny amount of PbI₂ was formed due to partial perovskite decomposition. The result of gas quenching and annealing treatment suppressed the formation of FAPbI₃-DMF intermediate phase, which is in line with the assumption that it appears within a cold sample as a metastable phase, and converts into the 2H hexagonal phase upon annealing.

5.5. OSC perovskite crystallization on bare glass substrates

The content in the following section shows the test measurements during OSC method in spin-coating chamber. For that purpose, the crystallization pathways of the compositions with different number of cations, namely MAPbI₃, MAPbBr₃, FA:MA, FA:MA:Cs, dissolved in a 4:1 DMF:DMSO solvent mixture, were studied during their growth on bare glass substrates. The usage of 20% DMSO within the precursor solution is conditioned by its role as a ligand, as it slows down the crystallization [15] and improves the quality of thin films. The deposition parameters were the same as in Sec. 5.2: 10 s at 1000 rpm and 30 s at 4000 rpm, while the results of this section are only partially comparable due to the differences in solvent mixtures and substrates.

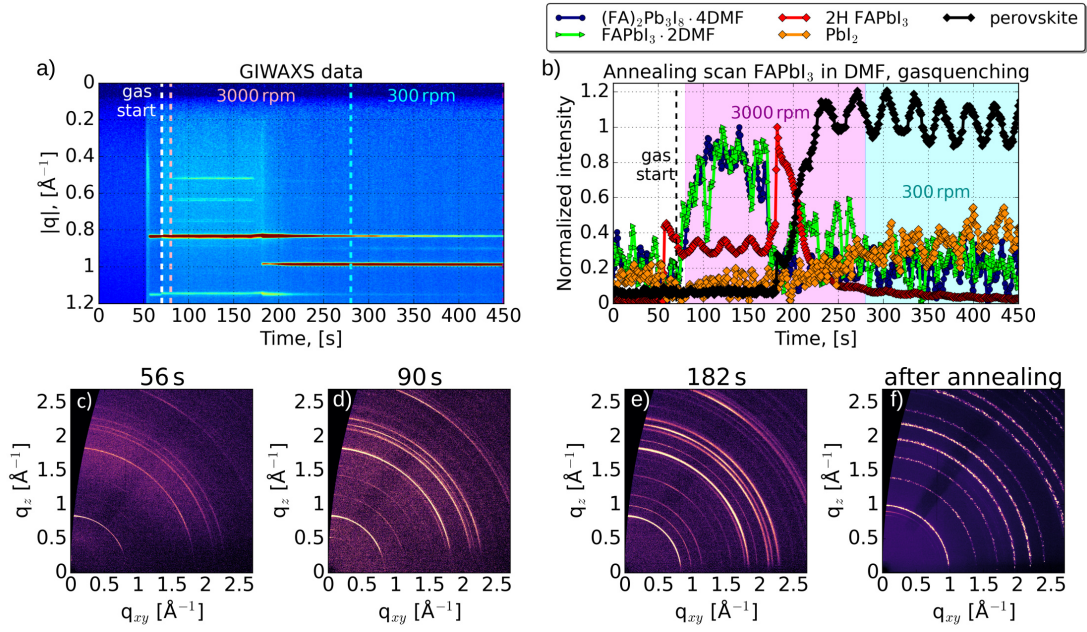


Figure 5.16.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during gas quenching- and annealing-assisted spin-coating of FAPbI₃ composition dissolved in DMF: (a) raw GIWAXS data in waterfall plot and (b) scattering intensity evolution of structures within the sample. Annealing was done for 430 s at 90 W starting at 20 s of the experiment, GIWAXS recording started at 50 s. Gas quenching with nitrogen stream of 35 l/min started at 70 s of the experiment, spinning started at 80 s at 3000 rpm for 120 s followed by spinning at 300 rpm for 280 s. Exemplary GIWAXS scans during (c), (d), (e) and (f) after annealing, diagonal shadow on the detector was created by a brass tube, used to supply nitrogen flow.

5.5.1. Formamidinium lead iodide

The crystallization of FAPbI₃ composition during the annealing treatment, tracked by GIWAXS, is displayed in Fig. 5.17. During the spin-coating procedure, no structures were detected within the deposited film. However, some of the 2H FAPbI₃ hexagonal phase [71], characterized by its reflection at $0.83 \text{ \AA}^{-1}$, was identified within the deposited thin film (Fig. 5.17(c)). The annealing treatment initiated solvent evaporation, resulting in an increase of 2H FAPbI₃ scattering intensity, which approached its maximum after 50 s of annealing at lamp power of 150 W, followed by a slow increase. After 120 s of annealing, the cubic perovskite phase scattering intensity started to increase, indicating the hexagonal-to-cubic transformation, within 30 s the cubic perovskite reflection approached maximum intensity and was then decreasing until the end of the experiment. Since no PbI₂ reflection was identified, this decrease was a result of the sample misalignment due to the thermal expansion of a double-sided sticky tape, used for sample fixation. The perovskite scattering intensity increased back to its maxima after switching off the halogen lamp, as the sample cooled down. The converted thin film showed the reflections from many crystallites due

to the poor coverage. Similarly to the previously discussed FAPbI_3 samples, it forms 2H hexagonal phase, which can be converted into the cubic perovskite phase only upon annealing.

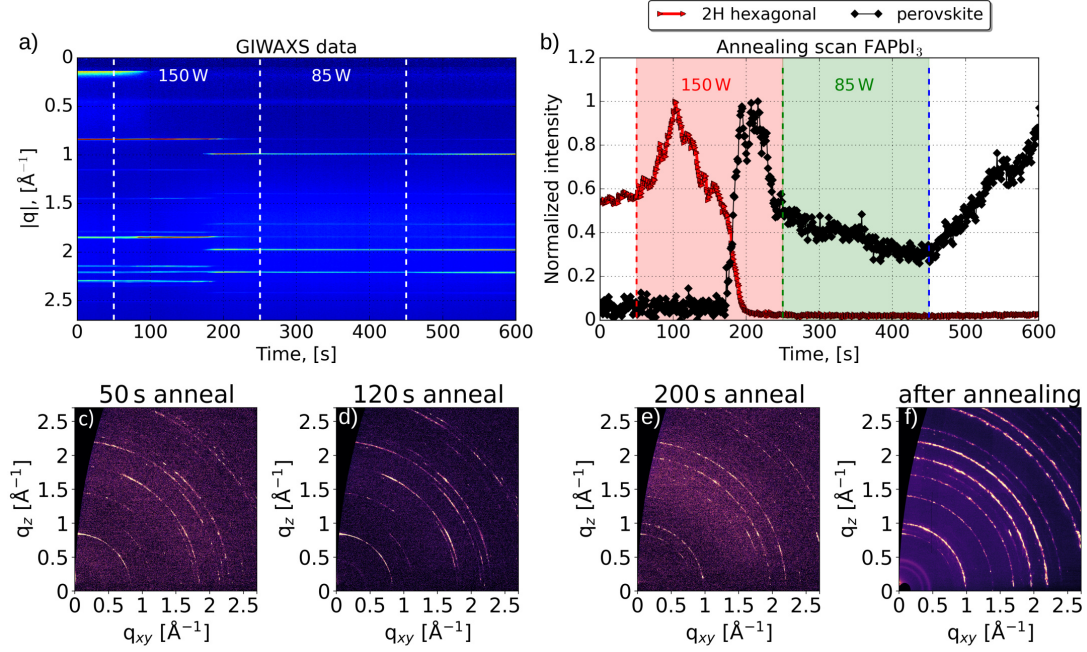


Figure 5.17.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during annealing step of FAPbI_3 composition: (a) raw GIWAXS data in waterfall plot and (b) scattering intensity evolution of structures within the sample. Annealing was done for 200 s at 150 W and 200 s at 85 W. Exemplary GIWAXS scans during (c), (d), (e) and (f) after annealing.

5.5.2. Methylammonium lead iodide

The crystallization of MAPbI_3 as the most applicable perovskite composition is displayed in Fig. 5.18. During the spin-coating procedure, X-ray scattering revealed the presence of randomly oriented molecules within the solution phase, characterized by the signal at $|q| = 0.50 \text{ \AA}^{-1}$ (Fig. 5.18(a)) without intermediate phases. Then, at 100 s of the spinning scan, corresponding to ~ 30 s after the spinning procedure, the $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ [152] intermediate phase scattering signal emerged at $0.45 \text{ \AA}^{-1}$, $0.51 \text{ \AA}^{-1}$ and $0.65 \text{ \AA}^{-1}$, similarly to the sample in Subsec. 5.2.3, compare Fig. 5.18(a,d) and Fig. 5.4(a). The formation presumably took place as a result of the solvent evaporation and thin film solidification, the scattering intensity increase slowed down towards the end of the spinning scan, i.e. within ~ 100 s, since the coated film got supersaturated.

Once the formation mechanism of the intermediate phase was identified, the spin-coated film was subsequently annealed by the halogen lamp with a golden reflector with the following parameters: 120 s at 150 W and 120 s at 85 W. Similarly to the sample,

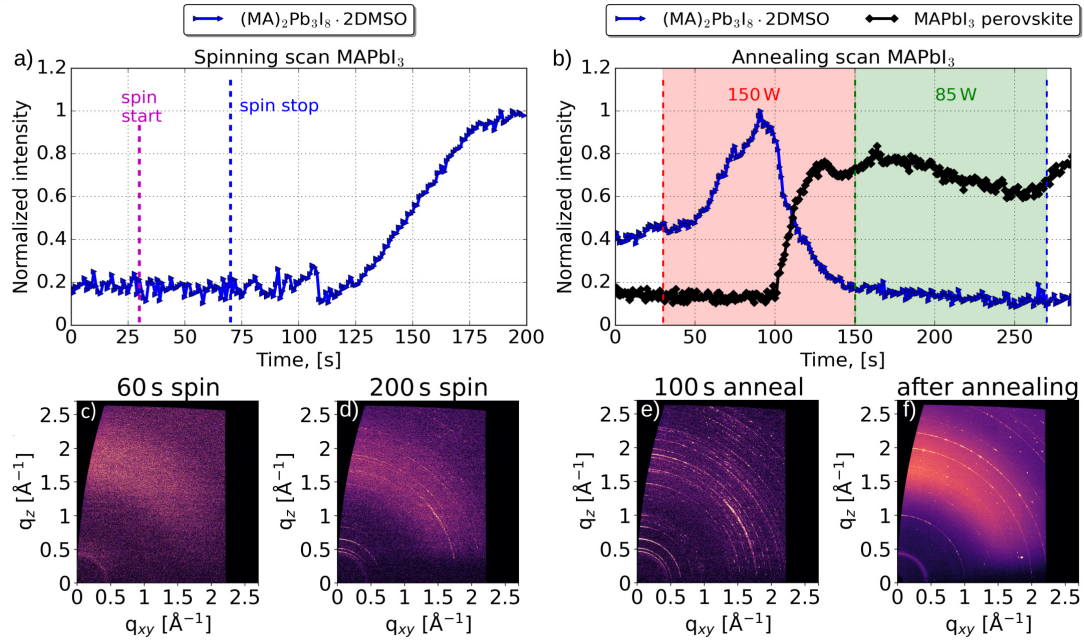


Figure 5.18.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) spin-coating and (b) annealing steps of MAPbI₃ perovskite thin film fabrication. Annealing was done for 120 s at 150 W and 120 s at 85 W. Exemplary GIWAXS scans (c) during and (d) after spin-coating, (e) during and (f) after annealing.

annealed by the hotplate, temperature increase resulted in scattering intensity increase of the intermediate phase (compare Fig. 5.4(c) and Fig. 5.18(b)), indicating fast solvent evaporation and crystallization. After ~60 s of the annealing procedure, the intermediate phase approached its maximum and was decreasing, ~10 s later, the perovskite phase scattering intensity, with the Bragg peak located at $1 \text{ \AA}^{-1}$, started to increase, indicating intermediate-to-perovskite conversion. Since the coverage of the sample is relatively poor due to the substrate (sticking coefficient to bare glass is lower than that for an ITO-coated glass), perovskite scattering intensity was slightly fluctuating between 130 s and 160 s of the experiment. The sample showed full conversion of the DMSO-based intermediate into the perovskite phase towards the end of the annealing procedure (Fig. 5.18(f)). This is an example of the most applicable MAPbI₃ composition growth by one-step method, this composition has a conversion temperature of 100°C, and does not form perovskite phase prior to annealing.

5.5.3. Methylammonium lead bromide

In contrast to the previously discussed composition, bromide-based MAPbBr₃ showed the presence of the cubic perovskite phase directly after spin-coating, as it can be seen in Fig. 5.6(c). The scattering intensity from perovskite phase, located at $\sim 1.06 \text{ \AA}^{-1}$, started to increase at 10 s of sample spinning, indicating the decrease of the thin film thickness

as a result of change in the rotation speed from 1000 rpm up to 3000 rpm. Only a small proportion of the crystallites were formed within the film, as it can be seen in Fig. 5.19(c). Directly after spinning, the solvent mixture started to evaporate, which led to an increase in perovskite scattering intensity, lasting until the end of the spinning scan (Fig. 5.19(d)). Moreover, it was identified that, during the spinning scan, the signal could be divided into two peaks, located at $|q| = 1.052 \text{ \AA}^{-1}$ and $|q| = 1.062 \text{ \AA}^{-1}$. This can be explained by the presence of MAPbBr₃ cubic perovskite structures with the standard [252] and bigger unit cells within one film.

The annealing initiated the reorientation and movement of the crystallites within the

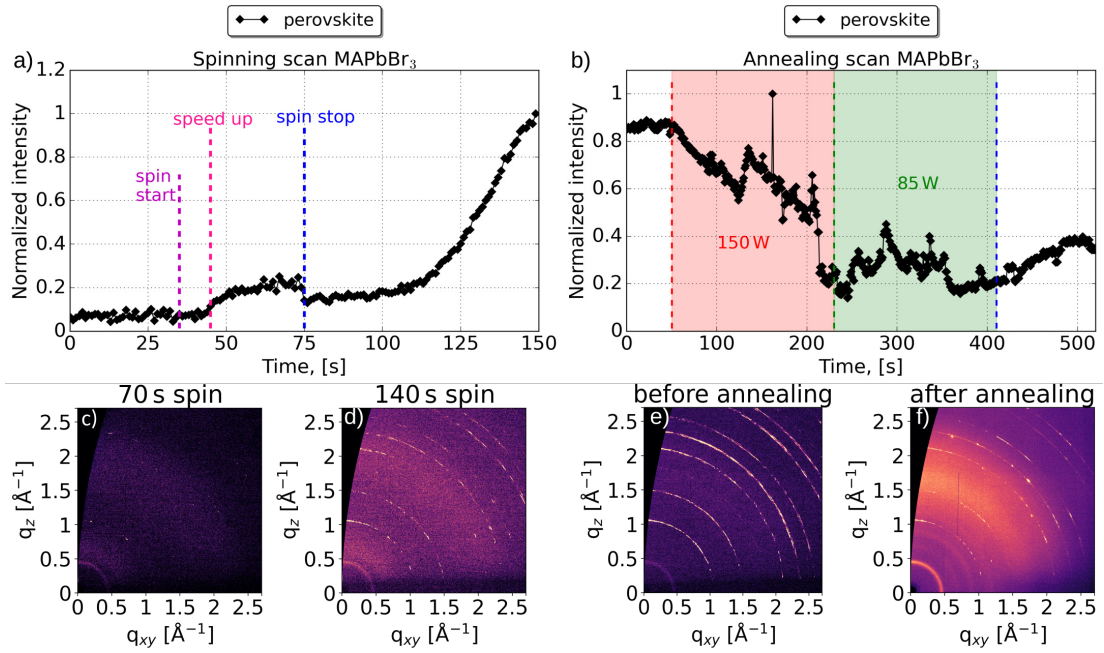


Figure 5.19.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) spin-coating and (b) annealing steps of MAPbBr₃ perovskite thin film fabrication. Annealing was done for 120 s at 150 W and 120 s at 85 W. Exemplary GIWAXS scans during (c), (d) spin-coating, (e) before and (f) after annealing.

sample (Fig. 5.27(a)), combined with the disappearance of some of them. The scattering intensity in the beginning and in the end of the annealing scan is displayed in Fig. 5.20. The annealing procedure merged both peaks, which appeared during spinning, into one, as in the end of the annealing scan it was located at $|q| = 1.058 \text{ \AA}^{-1}$ due to the thermal expansion. Once the sample was cooled down and realigned, this peak shifted to $|q| = 1.062 \text{ \AA}^{-1}$, which corresponds to the standard cubic lattice constant for MAPbBr₃ composition [252]. The difference between the scattering profiles from hot (red) and cooled (green) sample state was identified also in their FWHM, since at higher temperature a peak widening due to Debye-Waller effect takes place [253]. As a result, the peak width, which is inversely proportional to the coherently scattering island size, increased during

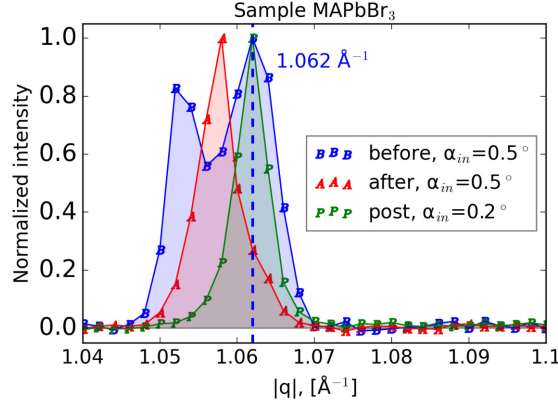
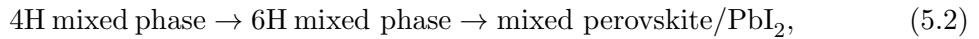


Figure 5.20.: Azimuthally integrated (100) MAPbBr₃ ring intensity of GIWAXS data at 0.5° angle of incidence corresponding to the scattering from the sample bulk before and after annealing treatment and final sample at 0.2° angle of incidence.

heat-induced treatment. The resulting perovskite phase displayed a preferred vertical orientation, characteristic for this composition (Fig. 5.30(a)).

5.5.4. Double cation sample FA:MA

The crystallization pathway of the most efficient double cation FA:MA composition, previously discussed in Subsec. 5.2.9, which includes 17% of MAPbBr₃ and 83% of FAPbI₃, is displayed in Fig. 5.21. The GIWAXS data before and shortly after the start of the annealing procedure had broad scattering features around 0.6 Å⁻¹ and 2.0 Å⁻¹ that correspond to the diffuse scattering from molecules and glass substrate, respectively. The annealing procedure initiated solvent evaporation followed by the identified crystallization sequence:



which is similar to the previously identified conversion diagram for double cation FA:MA composition, displayed in Fig. 5.11(b,c). The scattering intensities from the formed structures showed a similar spike-like increase, characteristic for the OSC method. The formation of the mixed perovskite phase mainly took place within the first ~180 s of annealing at 150 W based on the saturation of the scattering intensities from mixed hexagonal phases, and the only increasing scattering intensity from the PbI₂ phase [228], which is due to the heat-induced decomposition.

A remarkable difference arises from the absence of solvent-based intermediate phases, which is a consequence of no breaks between the spinning and annealing scans, while samples discussed in Sec. 5.2 were spin-coated in a conventional lab spin-coater, and then they were placed onto the hotplate at the diffractometer, which, in combination with the *ex situ* measurements of the precursor solution, resulted in a long delay before they

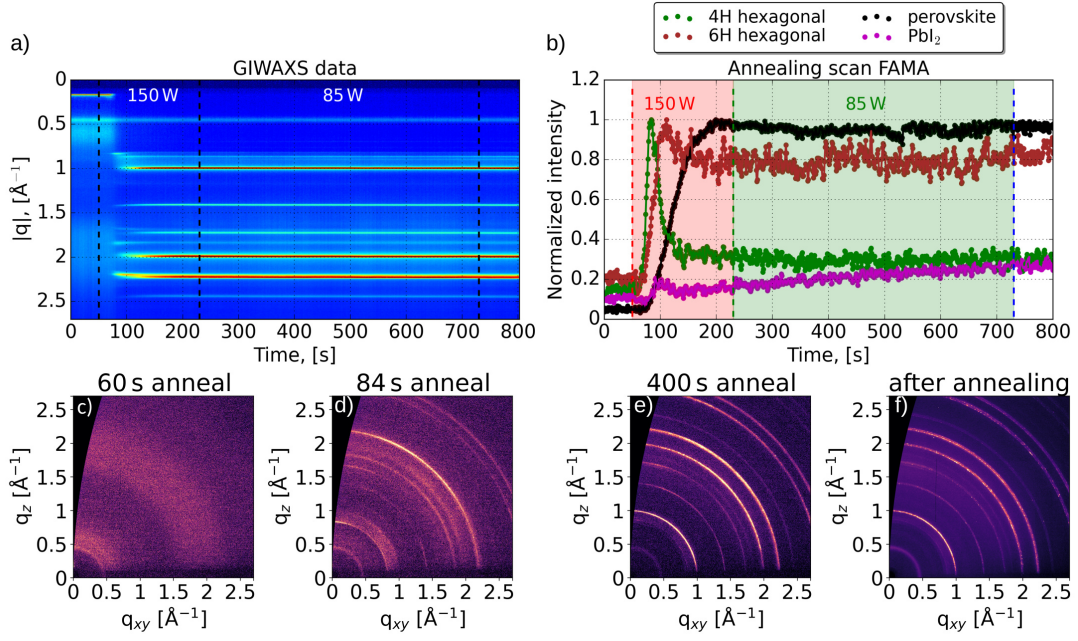


Figure 5.21.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during annealing step of FA:MA composition: (a) raw GIWAXS data in waterfall plot and (b) scattering intensity evolution of structures within the sample. Annealing was done for 180 s at 150 W and 500 s at 85 W. Exemplary GIWAXS scans during (c), (d), (e) and (f) after annealing.

were annealed. The final sample had some amounts of the 4H and 6H hexagonal phases, perovskite and a tiny fraction of the PbI_2 , as displayed in Fig. 5.22. The composition exhibited the same crystallization pathway during both hot plate annealing and NIR-based annealing. Additionally, the 4H hexagonal phase acted as an intermediate stage between the precursor solution and the mixed perovskite phase in both cases. This behavior may be attributed to the high bromide fraction present in the 4H hexagonal phase, which has a lower formation energy. [227].

5.5.5. Triple cation sample FA:MA:Cs

The effect of a 5% CsI addition to the FA:MA composition is shown in Fig. 5.23. The resulting composition, namely FA:MA:Cs, before annealing displayed the presence of broad features around $0.6 \text{ \AA}^{-1}$ and $2.0 \text{ \AA}^{-1}$ (Fig. 5.23(a,c)) that correspond to diffuse scattering from molecules and glass substrate, respectively.

The annealing procedure initiated rapid solvent evaporation and the appearance of the 4H hexagonal phase, characterized by the reflection at $0.825 \text{ \AA}^{-1}$, with a maximum intensity after ~ 30 s of the annealing procedure and mixed perovskite phase [71]. 4H hexagonal phase has then completely converted into the mixed perovskite phase, which is displayed in Fig. 5.23(b,d,e). This crystallization pathway supports the theory of the 4H hexagonal phase playing an essential role as an intermediate structure between the precursor

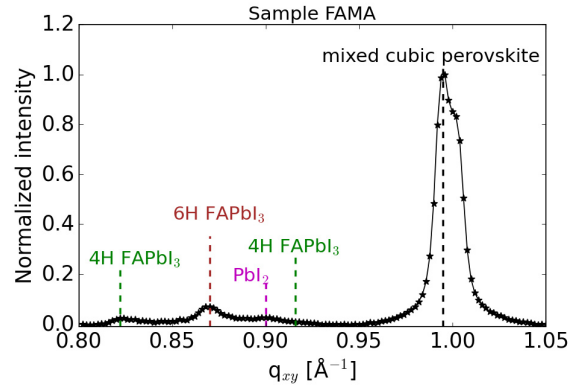


Figure 5.22.: Integrated intensity of *ex situ* GIWAXS scan from the FA:MA composition, deposited by one-step method, revealing the co-existence of cubic perovskite, 4H and 6H hexagonal phases, and PbI_2 , angle of incidence $\alpha_i = 0.2^\circ$.

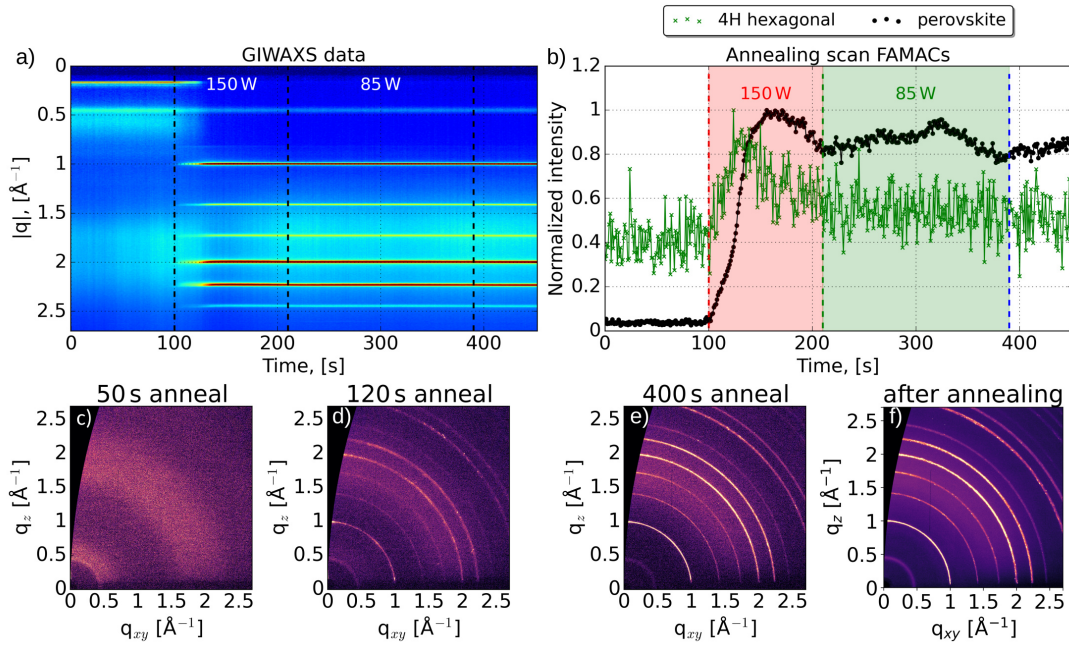


Figure 5.23.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during annealing step of FA:MA:Cs composition: (a) raw GIWAXS data in waterfall plot and (b) scattering intensity evolution of structures within the sample. Annealing was done for 110 s at 150 W and 180 s at 85 W. Exemplary GIWAXS scans (c) before; (d), (e) during and (f) after annealing.

phases and mixed perovskite phase. Similar tendency was observed in the case of multiple cation compositions, with two to four cations, deposited by OSC method, discussed in Subsec. 5.2.9, Subsec. 5.2.10, Subsec. 5.2.11 and Subsec. 5.5.4. The resulting film showed the presence of only mixed perovskite phase, which is an indicator of the positive effect of inorganic cation incorporation, while optimal annealing parameters excluded the presence of undesired phases.

Table 5.6.: Structural composition of the studied samples and solvents by the IPA-assisted method.

Sample	Solvent	Substrate
MAPbI ₃	DMF:DMSO (4:1)	Glass
FAPbI ₃	DMF:DMSO (4:1)	Glass
MAPbBr ₃	DMF:DMSO (4:1)	Glass
FA:MA	DMF:DMSO (4:1)	Glass
FA:MA:Cs	DMF:DMSO (4:1)	Glass

5.6. The effects of IPA antisolvent application on perovskite crystallization

The present section unravels the effects of antisolvent application on the crystallization pathways of different perovskite compositions. Solvent engineering was one of the ways to produce highly efficient perovskite solar cells [104]. In previous sections, details of the perovskite precursor solution-to-final film path *via* one-step deposition were discussed. It was found that in different compositions multiple intermediate compounds can appear due to the complexation. One of the ways to improve the quality of the studied films is antisolvent dripping [115] during the spin-coating procedure, typically 5 s before the spinning procedure is over (step 2 in Fig. 2.18). The introduction of the antisolvent-assisted method is provided in Subsec. 2.3.4 and is displayed in Fig. 2.18. In this section, samples with one to three cations and one or two halides will be studied during antisolvent-assisted deposition.

5.6.1. Methylammonium lead iodide

Present section demonstrates typical MAPbI₃ thin film growth on a bare glass substrate. In Fig. 5.24 the peak intensity evolution of the structures growing in the sample during (a) spin-coating and (b) annealing procedures in the following sequence: Fig. 5.24(c) displays the start of spinning indicating structural density increase with broad features around $0.6 \text{ \AA}^{-1}$ corresponding to scattering from a nearly amorphous precursor phase and $2 \text{ \AA}^{-1}$ related to the bare glass substrate signal. The antisolvent drop, displayed in Fig. 5.24(d), results in a fast intensity increase of an intermediate phase, namely the (MA)₂Pb₃I₈·2DMSO solvent complex [152]. Its scattering intensity was slowly increasing even after spin-coating, indicating the ongoing crystallization. The most remarkable effect of the IPA antisolvent application is the resulting horizontal preferred orientation of the DMSO-based intermediate phase.

The subsequent annealing process is illustrated in Fig. 5.24(b). The lamp power was 150 W for 120 s, followed by the heating at 85 W for 630 s. The annealing process led to the evaporation of excess solvent resulting in an increase in the intensity of diffraction rings at $0.45 \text{ \AA}^{-1}$, $0.51 \text{ \AA}^{-1}$ and $0.65 \text{ \AA}^{-1}$, which correspond to the Pb₃I₈ complex [152]

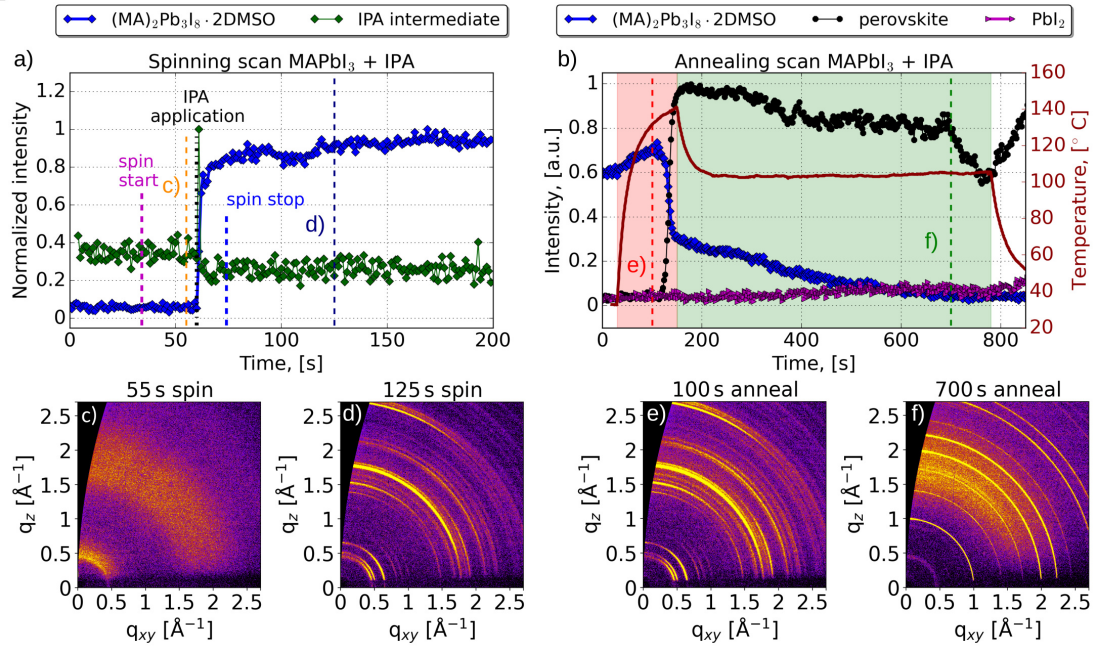


Figure 5.24.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) antisolvent-assisted spin-coating and (b) annealing steps of MAPbI₃ perovskite thin film fabrication. The dark red line in (b) shows the temperature of the glass substrate measured with a thermocouple at the same annealing parameters: 120 s at 150 W (red region) and 630 s at 85 W (green region). The vertical lines in the graphs correspond to the images (c)-(f). Exemplary GIWAXS scans (c) before and (d) after IPA application; (e) intermediate phase which is fully converted into (f) perovskite thin film with a tiny fraction of PbI₂ after annealing.

taking place until 120 s. Then, the intermediate phase converted in two steps into MAPbI₃ perovskite phase with an intense reflection at 1 Å⁻¹. The quick conversion presumably started near the surface, since the observed DMSO-based intermediate phase seeds can serve as nucleation centers to form 3D perovskite phase [254]. On the other side, due to the annealing nature of an IR heater, the bulk was crystallizing slower. After the full intermediate-to-cubic conversion, a small amount of PbI₂ with a reflection at 0.9 Å⁻¹ [228] was observed (Fig. 5.24(f)). The application of antisolvent led to a preferred vertical orientation of the perovskite phase (Fig. 5.30(b)).

5.6.2. Formamidinium lead iodide

The crystallization pathway of the IPA-assisted spin-coating of FAPbI₃ composition on a bare glass substrate during spinning and annealing stages is summarized in Fig. 5.25. During the spin-coating procedure, no sharp Bragg peaks were observed before the antisolvent application. The IPA drop resulted in the appearance of a templating vertically oriented structure, with its scattering signal at 0.54 Å⁻¹ (Fig. 5.25(d)). This structure, which is presumably FAI-PbI₂-x·DMSO [38] and commonly appears in samples with FA⁺ as a main cation, quickly converted into the highly-oriented 2H hexagonal FAPbI₃ phase (Fig. 5.25(a,c,d)). The annealing procedure took longer than that for the MAPbI₃ composition, as the power conversion efficiency of the solar cells, based on FAPbI₃, increases from 100°C up to ~150°C [255], since the full hexagonal-to-cubic perovskite conversion takes place at 150°C [219]. Due to the limitations, brought by the substrate-dependent annealing nature of the halogen lamp, the conversion of this composition was not completely captured by an X-ray beam: a partial conversion of hexagonal phase during the second annealing step is displayed in Fig. 5.25(b). With the onset of the annealing process, the scattering intensity from the hexagonal phase decreased. The intensity of the scattering reflection at 0.99 Å⁻¹, which is representative of the cubic perovskite phase, increased due to the hexagonal-to-cubic conversion. The resulting film showed cubic perovskite phase with tiny amounts of the hexagonal FAPbI₃ and PbI₂ (Fig. 5.25(f)). The resulting cubic perovskite showed random orientation, since during the annealing treatment, the hexagonal non-perovskite phase did not transfer its preferred orientation to the cubic perovskite phase, since it was a solid-solid transformation. In the past it was shown that the formation of the IPA-induced templating structure [38] leads to the presence of a preferred orientation for samples with FA as main cation. The present result suggests that the preferred orientation does not transfer between the solid phases, while it is beneficial for the FA-dominated compositions with the stabilized perovskite phase, such as FA:MA:Cs, discussed below, or a similar triple cation composition, studied previously [38].

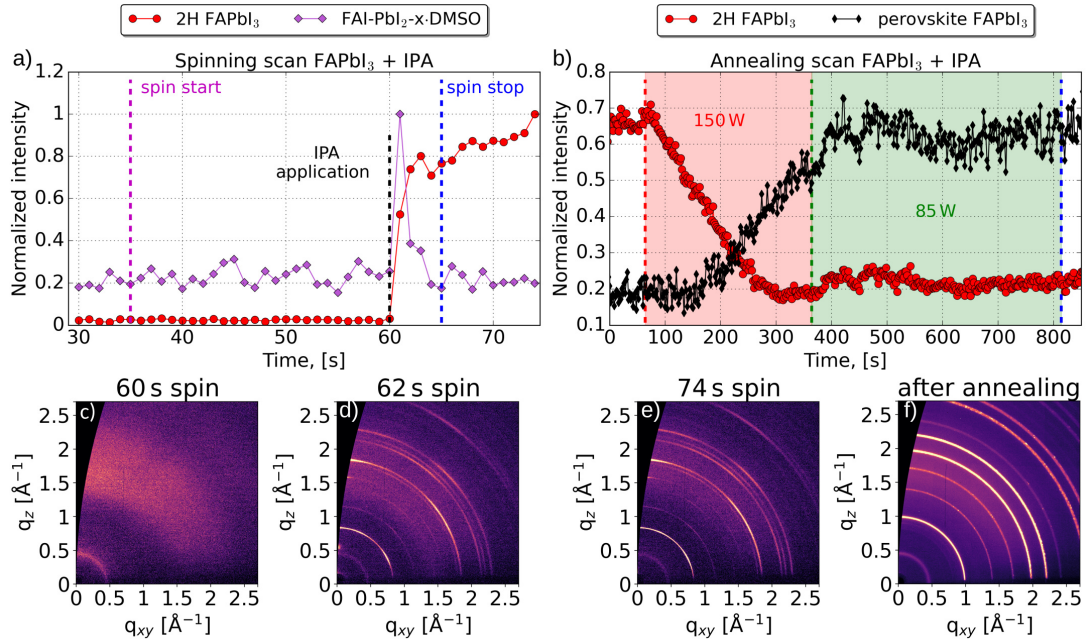


Figure 5.25.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) antisolvent-assisted spin-coating and (b) annealing steps of FAPbI₃ perovskite thin film fabrication. Annealing was done for 300 s at 150 W and 450 s at 85 W. Exemplary GIWAXS scans (c) before and (d), (e) after IPA application; (f) annealed film - perovskite thin film with tiny fractions of 2H hexagonal FAPbI₃ phase and PbI₂ after annealing.

5.6.3. Methylammonium lead bromide

The effect of an antisolvent application on MAPbBr₃ composition during fabrication is summarized in Fig. 5.26. Similarly to the previous single cation compositions, before the antisolvent application no sharp scattering features were observed. Once the antisolvent was applied, two bright reflections at $\sim 0.74 \text{ \AA}^{-1}$ and $1.41 \text{ \AA}^{-1}$ displayed rapid growth and then quickly vanished. The bright feature at $\sim 0.74 \text{ \AA}^{-1}$ might specifically correspond to the IPA, while the ring at $1.41 \text{ \AA}^{-1}$ is a liquid-phase related feature [28]. The application of IPA as an antisolvent led to the appearance of cubic perovskite phase with no intermediate phases. Similarly to the OSC method (Subsec. 5.2.5 and Fig. 5.6(a)), it is observed already during the IPA-assisted spin-coating. The clear effect of the IPA application is the appearance of a preferred orientation within the perovskite phase (Fig. 5.26(d)). Then, other brighter reflections on the perovskite diffraction rings got more visible, indicating the appearance of crystallites with random orientation.

During the annealing procedure, perovskite phase reflections could be fitted by two Gaussian peaks, located at $1.062 \text{ \AA}^{-1}$ and $1.06 \text{ \AA}^{-1}$. The scattering intensity of the peak at higher $|q|$ decreased, while the scattering intensity of the peak at lower $|q|$ increased during the annealing treatment. This might have happened due to thermal expansion of the thermal-resistant sticky tape during annealing process leading to the sample misalignment.

The final sample showed that the cubic perovskite reflection kept its maximum at $1.062 \text{ \AA}^{-1}$, which can be a consequence of the IPA antisolvent application fixing the unit cell parameter: it did not increase as in the case of OSC deposition, compare Fig. 5.28 and Fig. 5.7.

5.6.4. Summary on the effects of IPA antisolvent application on single cation compositions.

A direct comparison between samples grown with OSC method and IPA antisolvent-assisted deposition is shown in Fig. 5.29. For all antisolvent-assisted samples, a better coverage in comparison to the OSC samples was observed. For the MAPbI₃ composition, IPA antisolvent provided a preferred horizontal orientation to the (MA)₂Pb₃I₈·2DMSO intermediate phase, which converted into perovskite phase with a preferred vertical orientation. To FAPbI₃ composition. IPA antisolvent provided preferred orientation *via* the FAI:PbI_{2-x}DMSO templating structure [38] to 2H hexagonal FAPbI₃ phase, which then converted into the randomly oriented cubic perovskite phase. To the MAPbBr₃ composition, IPA antisolvent provided a preferred vertical orientation to the cubic perovskite, which remained through the annealing procedure. The results suggest a positive influence of IPA as an antisolvent, which ensures preferred vertical orientation to MA-based single cation perovskite compositions, since they either convert from the solvent-based intermediate phase (iodide), or directly form a cubic perovskite phase (bromide).

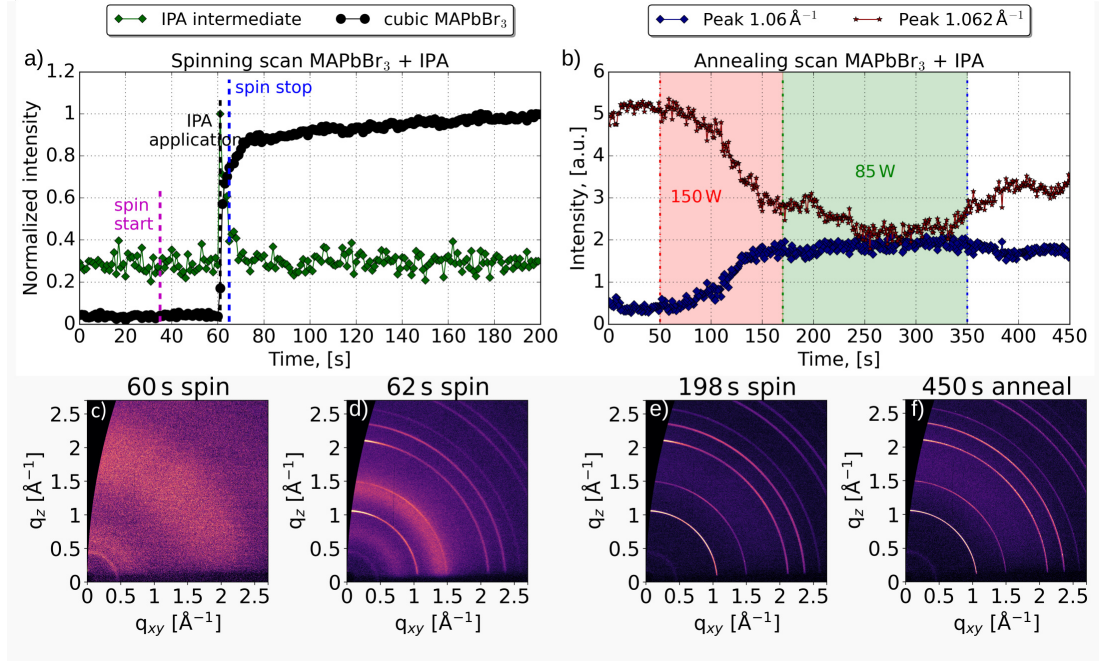


Figure 5.26.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) antisolvent-assisted spin-coating and (b) annealing steps of MAPbBr₃ perovskite thin film fabrication. Annealing was done for 120 s at 150 W and 180 s at 85 W. Exemplary GIWAXS scans (c) before and (d), (e) after IPA application; (f) MAPbBr₃ thin film after annealing, showing only cubic perovskite phase.

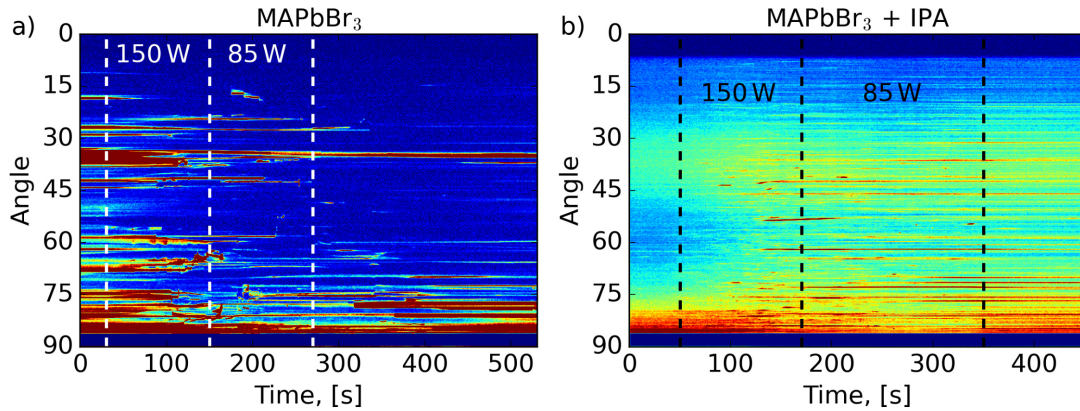


Figure 5.27.: Orientation profiles of cubic perovskite extracted from *in situ* GIWAXS during annealing steps of MAPbBr₃ composition (a) without and (b) with IPA antisolvent application. 0° corresponds to vertical orientation of the cubic perovskite phase.

5.6.5. Double cation sample FA:MA

The effect of IPA antisolvent application on the most efficient double cation composition, denoted as FA:MA, with precisely (FAPbI₃)_{0.83}(MAPbBr₃)_{0.17} composition, is summa-

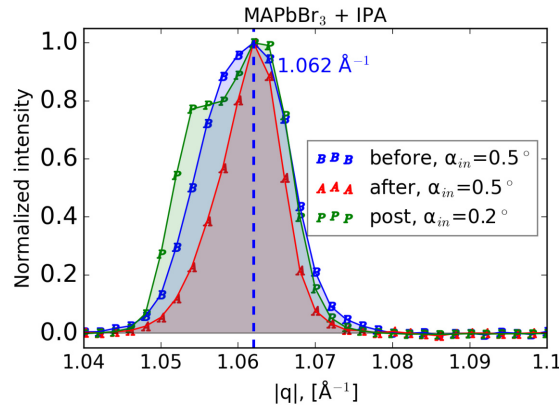


Figure 5.28.: Azimuthally integrated profiles of IPA-assisted (100) MAPbBr₃ GIWAXS data ring intensity at 0.5° angle of incidence corresponding to the scattering from the sample bulk before and after annealing treatment and final sample at 0.2° angle of incidence.

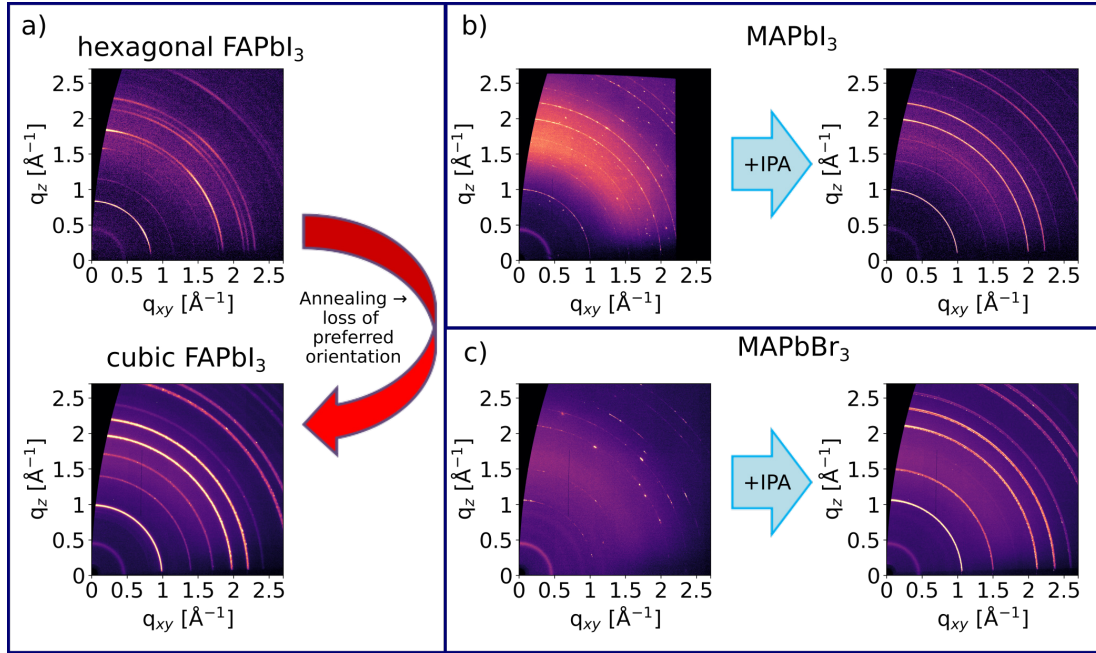


Figure 5.29.: Schematic summary of IPA antisolvent application on single cation compositions: (a) oriented 2H FAPbI₃ hexagonal phase converts into randomly oriented cubic FAPbI₃ perovskite; IPA improves the coverage of (b) MAPbI₃ and (c) MAPbBr₃, for the latter it provides a preferred orientation.

rized in Fig. 5.31. The following sample was deposited under a weak nitrogen flow, which prevented evaporation of the DMF solvent and provided conditions similar to the sample discussed in Subsec. 5.2.9.

Previously, FA:MA composition was studied with chlorobenzene as an antisolvent [116, 227]. Similarly to the compositions with only one cation, no scattering intensity from any intermediate structures was detected before the antisolvent application. The IPA drop

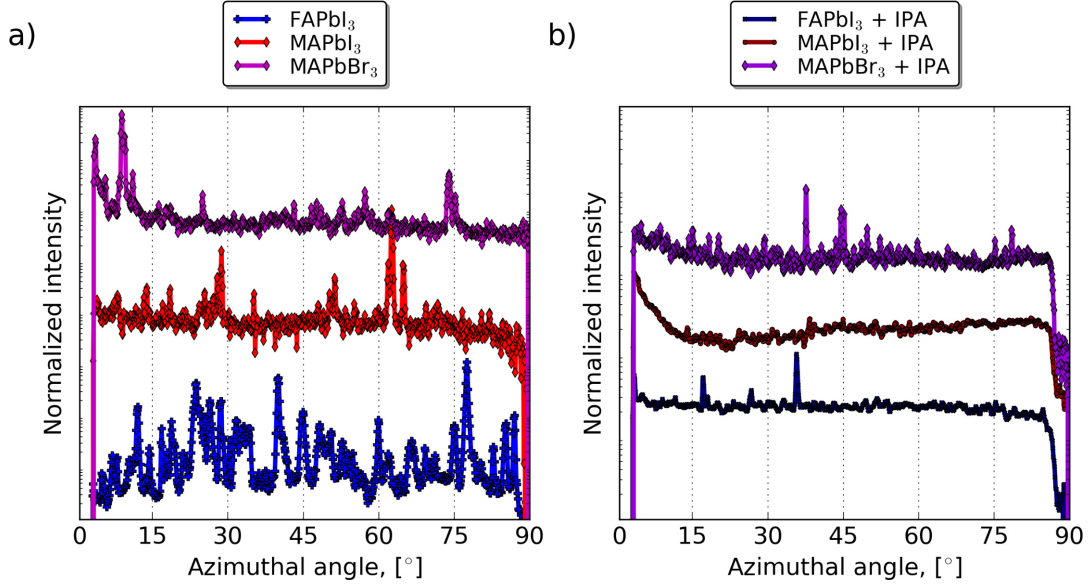


Figure 5.30.: Orientation profiles of cubic perovskite extracted from *ex situ* GIWAXS after annealing of FAPbI₃, MAPbI₃ and MAPbBr₃ compositions (a) without and (b) with IPA antisolvent application, 0° corresponds to the vertical orientation of cubic perovskite.

led to the appearance of a bright feature at $|q| = 0.54 \text{ \AA}^{-1}$, presumably corresponding to the scattering from an FAI:PbI₂-x-DMSO solvent complex [38] (Fig. 5.31(c)). Alongside with this structure, other additional bright reflections appeared at characteristic positions for 4H mixed hexagonal phase [71]. The feature at $|q| = 0.54 \text{ \AA}^{-1}$ disappears after ~ 2 s (Fig. 5.31(a)), while other bright reflections transform from more oriented into ring-like, compare Fig. 5.31(c) and Fig. 5.31(d). The application of IPA antisolvent lead to the appearance of a preferred orientation in FA-based structures, unlike random orientation in the case of OSC growth, observed in Fig. 5.10(a). Similarly to MAPbI₃ sample (Subsec. 5.6.1), a solvent complex (MA)₂Pb₃I₈·2DMSO [152] emerged 5 s after IPA application. Comparing Fig. 5.24(a) and Fig. 5.31(a), one should note that in the single cation MAPbI₃ composition DMSO-based solvent complex has appeared immediately after antisolvent application, while in the case of the FA:MA composition a 5 s delay between antisolvent application and DMSO-based phase growth took place, possibly caused by the appearance of the vertically oriented FAI:PbI₂-x-DMSO templating structure.

An additional intermediate, presumably FA_xMA_{1-x}PbI₃·DMF, characterized by the scattering signal at $|q| = 0.52 \text{ \AA}^{-1}$ appeared more than ~ 150 s after spin-coating of the thin film, during the break between the spinning and annealing scans, compare Fig. 5.31(d) and Fig. 5.31(e). This complex had bright scattering reflections along $q_{xy} = 0.5 \text{ \AA}^{-1}$ and $2 \text{ \AA}^{-1}$, which are also in line with the reflections from the DMF-based intermediate structure.

The annealing procedure initiated the conversion of both DMF- and DMSO-based in-

intermediate phases into 4H and 6H mixed hexagonal phases [71], mixed perovskite phase and a tiny amount of PbI_2 , similarly to FA:MA in OSC (conversion diagram Fig. 5.11(c) in Subsec. 5.2.9). The clear effect of an antisolvent application could be seen in conversion times, since for the DMF-based intermediate it was 60 s instead of 45 s in OSC case, while for the DMSO-based intermediate phase it was 95 s instead of 250 s. This might be a consequence of the formation of the FA-based complex as a result of an IPA antisolvent application, which lead to a higher amount of the FAI and DMF-based intermediate phase within the coated film and the appearance of the preferred orientation of the DMF-based intermediate. A faster conversion of the DMSO-based intermediate can be assigned to a smaller fraction of the MA-based complex within the spin-coated film. The resulting preferred orientation for the FA:MA composition by IPA-assisted deposition was at 77.5° , 53° and 0° (Fig. 5.33(b)). The latter angle coincides with the preferred orientation of the IPA-assisted single cation MAPbI_3 and MAPbBr_3 compositions, displayed in Fig. 5.30(b). This leads to the assumption that the preferred vertical orientation of the mixed perovskite phase in the FA:MA composition is an effect of the MA cation, while the preferred orientations at 12.5° and 37° is influenced by the FAI-DMSO templating structure [38].

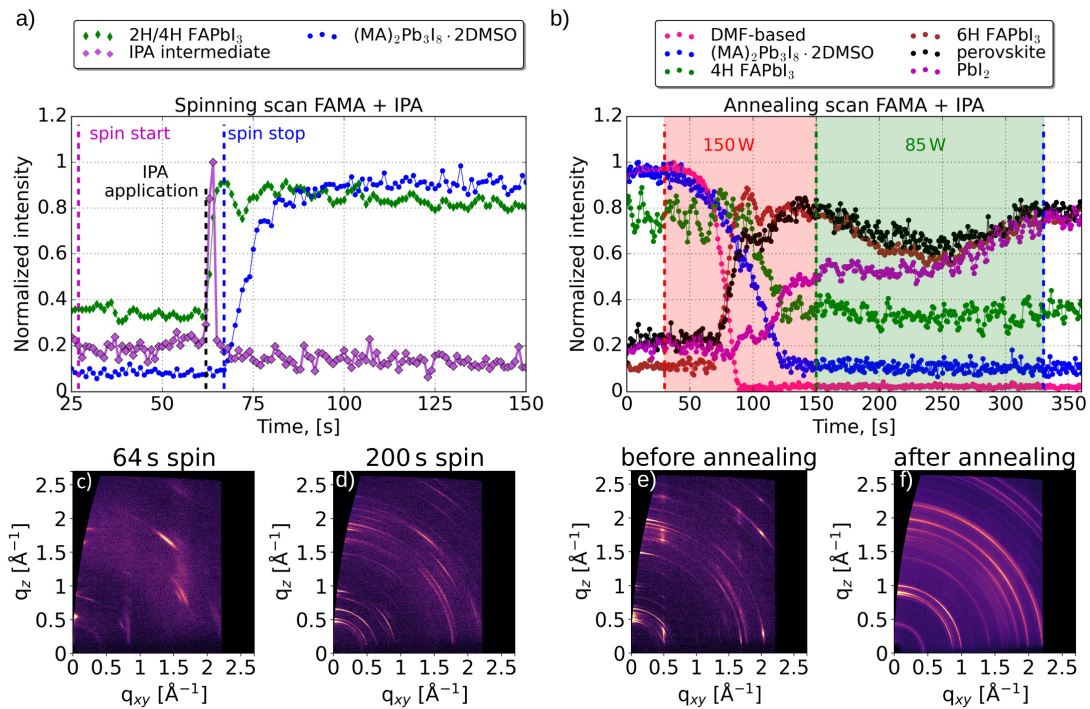


Figure 5.31.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) antisolvent-assisted spin-coating and (b) annealing steps of FA:MA perovskite thin film fabrication. Annealing was done for 120 s at 150 W and 180 s at 85 W. Exemplary GIWAXS scans (c), (d) after IPA application, (e) before and (f) after annealing.

5.6.6. Triple cation sample FA:MA:Cs

Following the research on the effects of an antisolvent application, a triple cation composition, namely FA:MA:Cs, same as in Subsec. 5.2.10 was investigated, its data is summarized in Fig. 5.32. The results are similar to the published research [38]. In particular, IPA antisolvent application immediately initiated the formation of the FAI:PbI₂-x-DMSO templating structure and 4H mixed hexagonal phase. The FAI-DMSO solvent complex scattering intensity rapidly decreased, while other DMSO-based intermediate phase, namely (MA)₂Pb₃I₈·2DMSO [152], started its growth. The 4H mixed hexagonal phase was slowly converting into the mixed perovskite phase. The studied FA:MA:Cs composition by its nature, due to the stabilization effect of Cs⁺ cations, shows the presence of the mixed perovskite phase before annealing. This allows IPA antisolvent to provide a preferred orientation directly to the desired mixed perovskite phase during the spin-coating procedure (Fig. 5.32(d)).

The annealing procedure initiated the conversion of the (MA)₂Pb₃I₈·2DMSO phase,

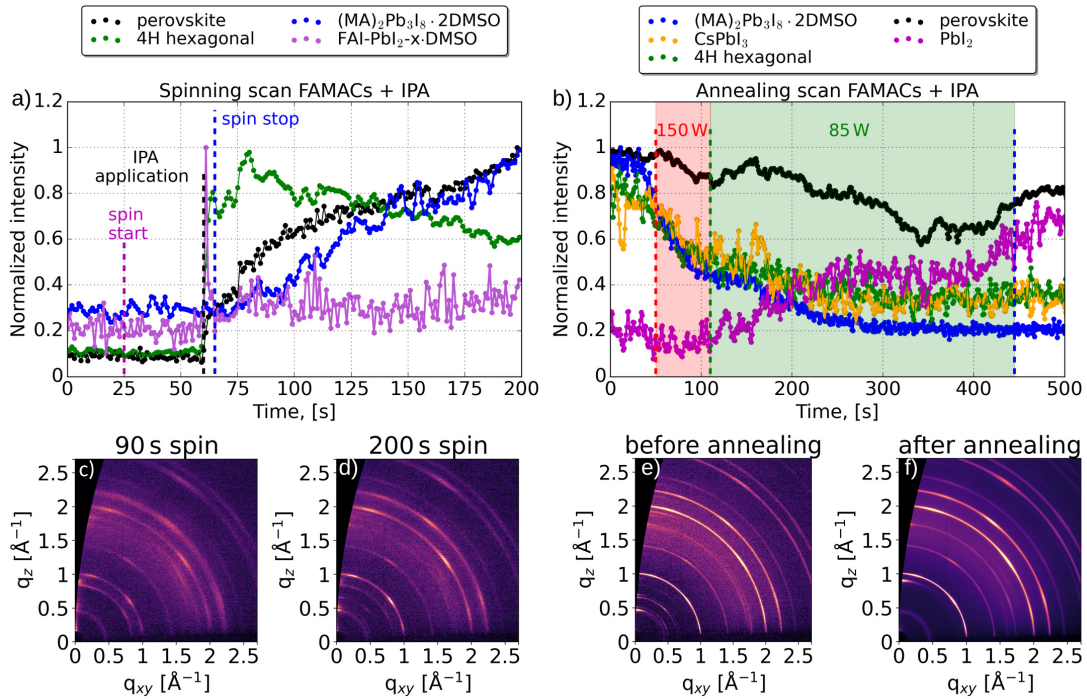


Figure 5.32.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) antisolvent-assisted spin-coating and (b) annealing steps of FA:MA:Cs perovskite thin film fabrication. Annealing was done for 60s at 150 W and 335s at 85 W. Exemplary GIWAXS scans (c), (d) after IPA application, (e) before and (f) after annealing.

an orthorhombic CsPbI₃ phase [156] characterized by the Bragg peak at 0.7 Å⁻¹, and 4H mixed hexagonal phase into mixed perovskite phase and some of PbI₂ due to overheating, which took place 300 s into the annealing scan (Fig. 5.32(b,e,f)). The remarkable influence

of antisolvent application during spin-coating is the presence of a preferred orientation for the mixed perovskite phase, which stays for this structure during the annealing treatment.

5.6.7. Summary on the effects of IPA antisolvent application on mixed cation compositions

A direct comparison between perovskite orientations of samples with OSC method and IPA antisolvent-assisted deposition is shown in Fig. 5.33. IPA antisolvent application improves thin film coverage, which results in more consistent intensity distribution along perovskite phase scattering rings for samples with mixed compositions. Moreover, IPA gives a preferred orientation to mixed perovskite phases at angles 77.5° and 53° , while the third orientation was different: 0° for FA:MA and 14° for FA:MA:Cs. Antisolvent provided the preferred orientation *via* FAI:PbI_{2-x}DMSO templating structure [38] to dissimilar structures in different compositions: in FA:MA it was given to the 4H mixed hexagonal phase, while in the case of the FA:MA:Cs composition it was provided directly to the mixed perovskite phase. Nevertheless, similarities in the perovskite preferred orientation can be explained by the influence of FA cations, while in the case of FA:MA composition, its vertical orientation comes from the MA cation. The origins of the preferred orientation at 14° is discussed in the next sections: an effect of 5% CsI incorporation into single cation compositions is studied during the one-step spin-coating and IPA antisolvent-assisted growth.

Another effect of IPA antisolvent application on mixed perovskite in triple cation

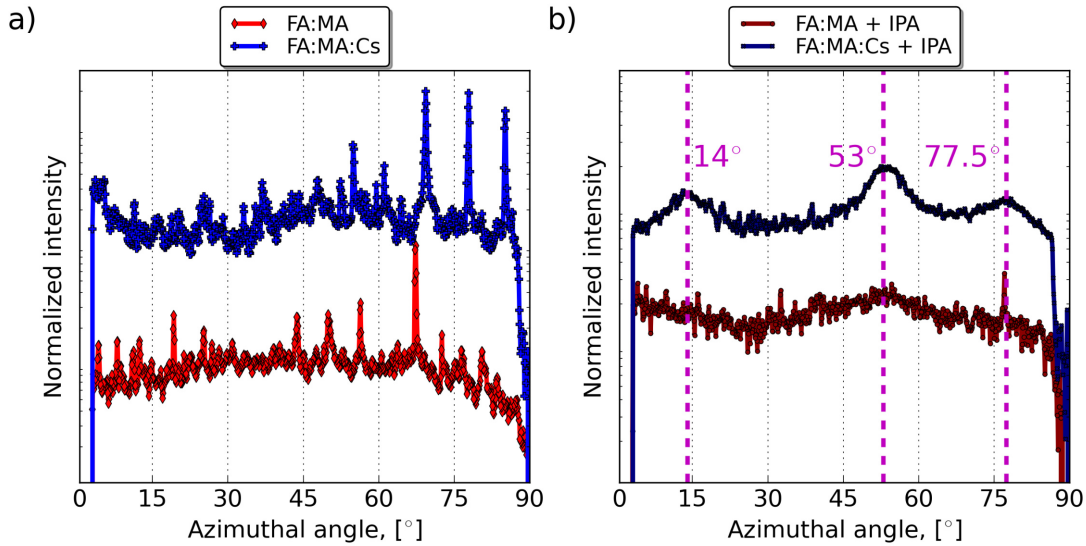


Figure 5.33.: Orientation profiles of cubic perovskite phase extracted from *ex situ* GIWAXS after annealing of FA:MA and FA:MA:Cs compositions (a) without and (b) with IPA antisolvent application, 0° corresponds to the vertical orientation of cubic perovskite.

FA:MA:Cs composition is summarized in Fig. 5.34. In the case of one-step method, cubic perovskite was formed during the annealing process, comparing its integrated scattering

intensity profiles at 150 s (maximum intensity) and 450 s (after annealing) one can observe a shift of the Bragg peak position from $0.998 \text{ \AA}^{-1}$ to $1 \text{ \AA}^{-1}$, while for antisolvent-assisted sample cubic perovskite maximum moved from $1 \text{ \AA}^{-1}$ to $1.004 \text{ \AA}^{-1}$. This difference might be a consequence of faster crystallization, since for the one-step method, perovskite phase appeared only during the annealing procedure, while for IPA-assisted method it was formed immediately after the antisolvent application, which initiated DMSO-based solvent complex formation. A strong change in the reflection position from the perovskite phase in an antisolvent-assisted sample indicates a successful incorporation of Cs cations into the perovskite network, produced prior to annealing.

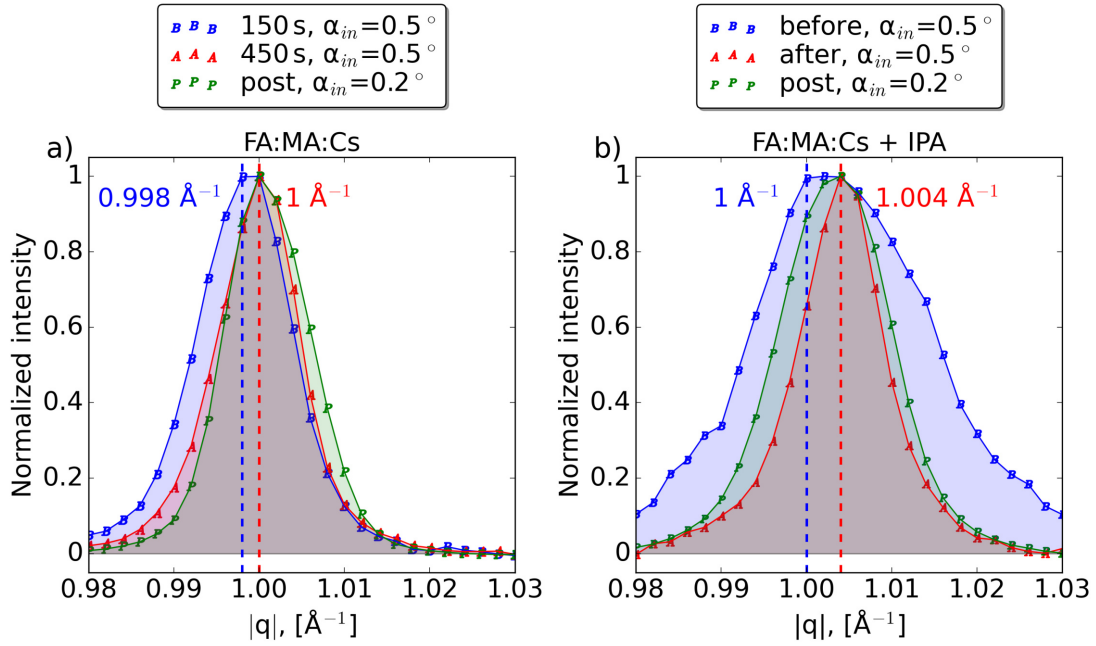


Figure 5.34.: Azimuthally integrated profiles of (100) mixed perovskite phase GIWAXS reflection for (a) FA:MA:Cs by one-step method, measured at 150 s, 450 s of annealing at $\alpha_i = 0.5^\circ$, post indicates final sample measured at $\alpha_i = 0.3^\circ$; (b) FA:MA:Cs by IPA antisolvent-assisted method: before and after annealing measured at $\alpha_i = 0.5^\circ$, post indicates final sample at $\alpha_i = 0.3^\circ$.

5.7. Effects of cesium incorporation on perovskite crystallization

The drawbacks of perovskite photo- [256] and moisture [257] stability led to compositional engineering, including inorganic cation incorporation, such as Cs^+ or Rb^+ [258], which can improve the thin film morphology [259]. This section demonstrates the influence of 5% CsI incorporation into single cation perovskite compositions, namely into MAPbI_3 , FAPbI_3 and MAPbBr_3 , during OSC and IPA antisolvent application.

Table 5.7.: Structural composition of the studied samples and solvents.

Sample	Solvent	Substrate
$(\text{MAPbBr}_3)_{0.95}\text{CsI}_{0.05}$	DMF:DMSO (4:1)	Glass
$(\text{FAPbI}_3)_{0.95}\text{CsI}_{0.05}$	DMF:DMSO (4:1)	Glass
$(\text{MAPbI}_3)_{0.95}\text{CsI}_{0.05}$	DMF:DMSO (4:1)	Glass

5.7.1. Methylammonium lead iodide + CsI

The GIWAXS data of $(\text{MAPbI}_3)_{0.95}(\text{CsI})_{0.05}$ and scattering intensity from different structures during annealing are displayed in Fig. 5.35(a,c,d). The formation of the solvent-based $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ intermediate phase [152] was not identified during the spinning scan, only directly before annealing, unlike for the pure MAPbI_3 composition (Subsec. 5.5.2), where the formation was observed directly after spinning (Fig. 5.18(a)). This might be a direct suppression of the MA-based intermediate phase formation due to the presence of CsI. This intermediate phase was randomly oriented, which is typical for the OSC fabrication procedure of MAPbI_3 composition without organic additives.

The solvent evaporation before annealing treatment resulted in intermediate phase

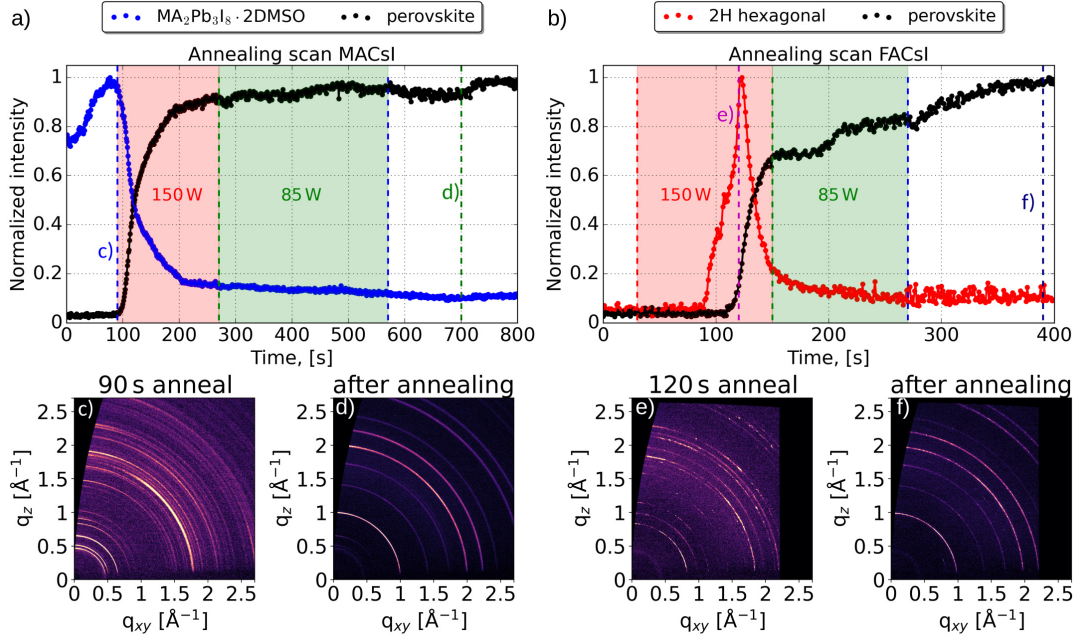


Figure 5.35.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during annealing step of (a) $\text{MAPbI}_3 + \text{CsI}$ and (b) $\text{FAPbI}_3 + \text{CsI}$ perovskite thin film fabrication. Annealing was done for: (a) 180 s at 150 W and 300 s at 85 W, (b) 120 s at 150 W and 120 s at 85 W. Exemplary GIWAXS scans during (c) $\text{MAPbI}_3 + \text{CsI}$, (e) $\text{FAPbI}_3 + \text{CsI}$ and after (d) $\text{MAPbI}_3 + \text{CsI}$, (f) $\text{FAPbI}_3 + \text{CsI}$ annealing.

scattering increase (Fig. 5.35(a)), which indicated thin film solidification process. The annealing procedure immediately initiated intermediate-to-perovskite conversion, unlike for

the pure MAPbI₃ composition, where annealing initiated intermediate phase scattering increase (Subsec. 5.2.3). The resulting film showed preferred orientation, this indicates the direct influence of 5% CsI on cubic perovskite structure, which was found previously for 10% of CsI for gas-assisted thin films [257]. Another positive influence of Cs inorganic cation incorporation is the improvement of the thin film coverage even on the bare glass substrate, in comparison to the pure MAPbI₃ composition manufactured by OSC method, which was shown in Subsec. 5.2.3.

5.7.2. Formamidinium lead iodide + CsI

Since FAPbI₃ composition has a large tolerance factor and is more stable in 2H hexagonal phase at room temperature, it can be alloyed with CsPbI₃, which has a small tolerance factor and stabilized to an orthorhombic δ -CsPbI₃ phase [135, 144]. The incorporation of 10% Cs into FAPbI₃ composition significantly improves moisture and photostability [260], since Cs prevents black-to-yellow transition in high humidity environments due to the better stability of inorganic cations and reduced tolerance factor.

The GIWAXS data of (FAPbI₃)_{0.95}(CsI)_{0.05} and scattering intensity from different structures during annealing are displayed in Fig. 5.35(b,e,f). The annealing procedure initiated precursor solution evaporation, followed by 2H hexagonal FAPbI₃ phase formation, it reached its scattering maxima at ~ 90 s of the annealing treatment, while perovskite scattering intensity started its growth after ~ 80 s of annealing. After approaching its maximum, the 2H hexagonal phase simultaneously [251] and rapidly transformed into the perovskite phase (Fig. 5.35(b,e)). The simultaneous nature of the phase transformation indicates a successful incorporation of Cs cations into the mixed perovskite phase and optimization of the tolerance factor. Similarly to the case of MAPbI₃ composition, the addition of 5% Cs resulted in an improved thin film coverage and led to the appearance of the preferred orientation for the perovskite phase (Fig. 5.35(f)). A comparison of cubic perovskite angular distributions with and without addition of Cs into MAPbI₃ and FAPbI₃ is displayed in Fig. 5.42.

5.7.3. The effect of IPA antisolvent application during MAPbI₃ + CsI crystallization

The effect of an antisolvent application on the composition with mixed cations, namely (MAPbI₃)_{0.95}(CsI)_{0.05}, is summarized in Fig. 5.36. No scattering features were observed prior to antisolvent application, as with other IPA-assisted single cation compositions. Once IPA was applied, two bright rings at $\sim 0.74 \text{ \AA}^{-1}$ and $1.41 \text{ \AA}^{-1}$ were identified and then quickly vanished (Fig. 5.36(c)). The bright feature at $\sim 0.74 \text{ \AA}^{-1}$ might specifically correspond to the IPA-DMSO complex, while the ring at $1.41 \text{ \AA}^{-1}$ is a broad liquid-phase related feature [28]. The IPA-based structure rapidly converted into the DMSO-based intermediate phase, which consequently saturated after 60 s (Fig. 5.36(a)). This is a positive

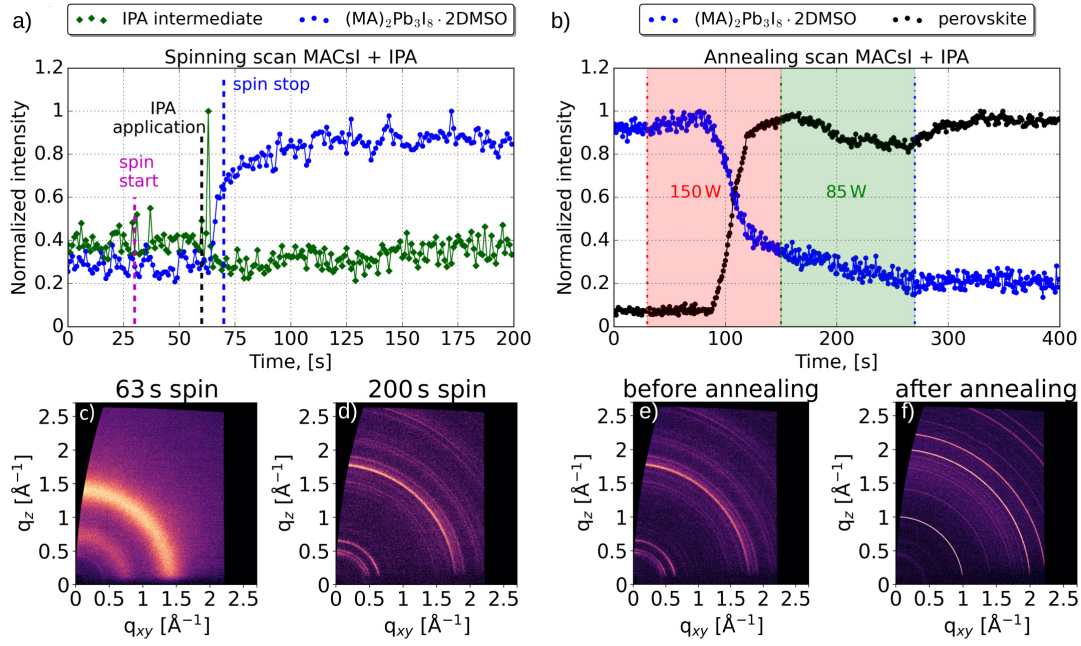


Figure 5.36.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) antisolvent-assisted spin-coating and (b) annealing steps of MAPbI₃ + CsI perovskite thin film fabrication. Annealing was done for 120 s at 150 W and 120 s at 85 W. Exemplary GIWAXS scans (c), (d) after IPA application, (e) before and (f) after annealing.

influence of the antisolvent application, since it initiates an intermediate phase formation, which serves as nucleation centers to form perovskite phase [254].

The annealing procedure partially evaporated the solvent, which led to (MA)₂Pb₃I₈·2DMSO intermediate phase scattering intensity increase lasting 60 s, followed by rapid conversion into cubic MAPbI₃ perovskite until the end of the annealing scan (Fig. 5.36(b)). The final sample showed the presence of a tiny amount of unreacted δ -CsPbI₃ phase, characterized by a scattering signal at $\sim 0.70 \text{ \AA}^{-1}$ [156] and mainly perovskite MAPbI₃ phase, which means that premixed CsI has been at least partially coordinated [261] with PbI₂. The combination of CsI incorporation and IPA antisolvent application provided some preferred orientation to the perovskite phase at 28°.

5.7.4. The effect of IPA antisolvent application during FAPbI₃ + CsI crystallization

The effect of an antisolvent application on (FAPbI₃)_{0.95}CsI_{0.05} composition is summarized in Fig. 5.37. Before the antisolvent was dropped, no sharp scattering features were observed, while IPA application resulted in the appearance of both IPA-based intermediate, characterized by the reflection at $\sim 0.74 \text{ \AA}^{-1}$, the same as in the MA-based antisolvent-assisted compositions, and a small amount of the FAI:PbI₂-x·DMSO templating structure

with its scattering reflection at $\sim 0.54 \text{ \AA}^{-1}$ [38].

The IPA-based structure rapidly converted into the 2H hexagonal FAPbI₃ phase and DMSO-based templating structure, the latter phase slowly converted into the 2H hexagonal phase until the end of the spinning scan, characterized by simultaneous scattering decrease and increase, respectively (Fig. 5.37(a)). This is one of the direct impacts of CsI addition into FAPbI₃: only 5% are already capable of suppressing the ability of FA to form a preferred orientation through templating structure formation due to antisolvent application, since the IPA-based intermediate phase, typically formed for FA-free compositions, is also based on DMSO.

The annealing was done in two steps, due to the complexity, resulting from the hexago-

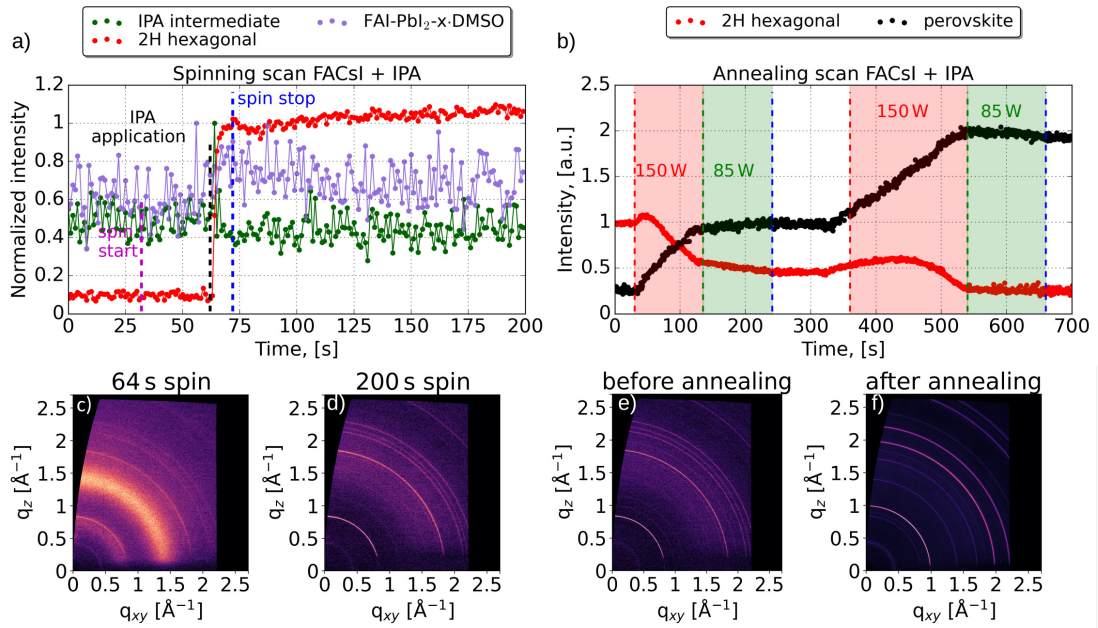


Figure 5.37.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) antisolvent-assisted spin-coating and (b) annealing steps of FAPbI₃ + CsI perovskite thin film fabrication. Annealing was done for 60 s at 150 W and 335 s at 85 W. Exemplary GIWAXS scans (c), (d) after IPA application, (e) before and (f) after annealing.

nal phase formation during spin-coating procedure: a potential CsI incorporation into the 2H FAPbI₃ matrix drastically increased the conversion temperature, since it is $\sim 300^\circ\text{C}$ for the pure CsPbI₃ composition [156]. The first annealing step initiated solvent evaporation, resulting in a tiny increase of the scattering intensity from the 2H hexagonal FAPbI₃ phase, which then partially converted into the perovskite phase. The antisolvent application ensured better thin film coverage in comparison to the one-step method, which meant that there was more material to convert. The second annealing step was successful, the final film had cubic perovskite phase. Besides that, the application of IPA as an antisolvent resulted in the appearance of the preferred orientation for the perovskite phase. For

(FAPbI₃)_{0.95}CsI_{0.05}, the resulting orientation was 45°, as displayed in Fig. 5.42(b).

5.7.5. Methylammonium lead bromide + CsI

Previous research reported the successful incorporation of Cs into the MAPbBr₃ composition, which resulted in improved structural and photophysical properties, such as orientational ordering of MA cations and higher moisture stability [262]. The GIWAXS data of (MAPbBr₃)_{0.95}(CsI)_{0.05} and scattering intensity evolution of the cubic perovskite phase during spin-coating and annealing are displayed in Fig. 5.38. Perovskite scattering intensity started to increase 30 s after spinning start, as a result of solvent evaporation. This crystallization was similar to the previously discussed MAPbBr₃, deposited by one-step method (Fig. 5.19(a)). Only from a small number of crystallites a scattering signal was visible, due to the poor coverage of bare glass substrate. Perovskite phase formation lasted until the end of the spinning scan, indicating solvent evaporation from the coated film.

The annealing treatment initiated further solvent evaporation and cubic perovskite

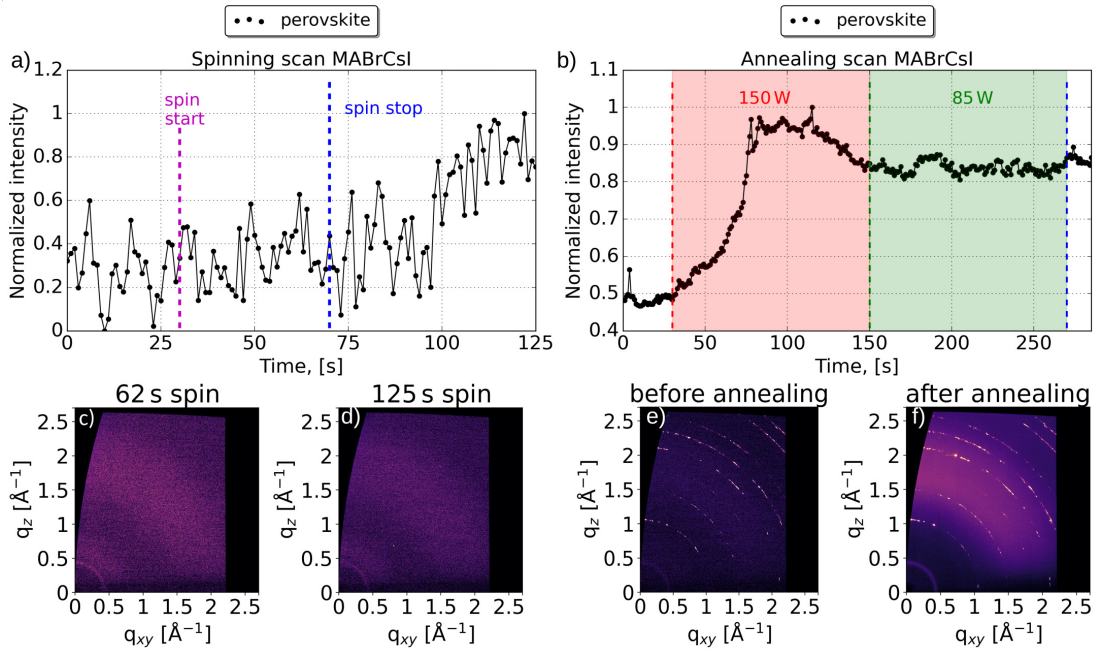


Figure 5.38.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) spin-coating and (b) annealing steps of MAPbBr₃ + CsI perovskite thin film fabrication. Annealing was done for 60 s at 150 W and 335 s at 85 W. Exemplary GIWAXS scans (c), (d) after IPA application, (e) before and (f) after annealing.

formation, comparable to CsI-free MAPbBr₃ samples (Subsec. 5.2.5 and Subsec. 5.5.3). The perovskite phase scattering intensity increased during the annealing treatment, which reflected perovskite phase crystallization (Fig. 5.38(b)). The resulting thin film demonstrated the (100) reflection from the perovskite phase at 1.062 Å⁻¹, which indicated an

incomplete incorporation of CsI into the MAPbBr₃ composition, as it can be seen in Fig. 5.39(a).

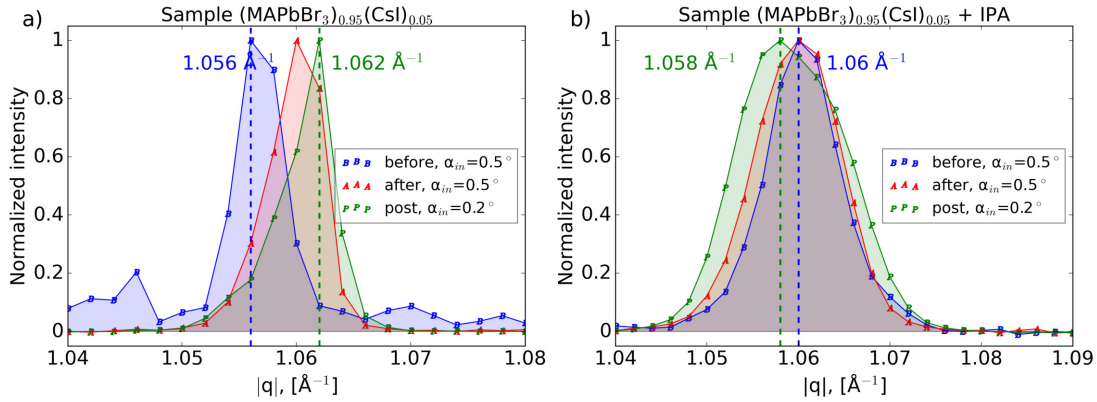


Figure 5.39.: Azimuthally integrated profiles of (100) MAPbBr₃ GIWAXS reflection for (a) (MAPbBr₃)_{0.95}(CsI)_{0.05} and (b) (MAPbBr₃)_{0.95}(CsI)_{0.05} + IPA: before and after annealing measured at 0.5° angle of incidence corresponding to the scattering from the sample bulk, post indicates final sample at 0.3° angle of incidence.

5.7.6. The effect of IPA antisolvent application during MAPbBr₃ + CsI crystallization

The GIWAXS data of (MAPbBr₃)_{0.95}(CsI)_{0.05} and scattering intensity evolution of the cubic perovskite during IPA-assisted spin-coating and annealing are displayed in Fig. 5.40. Similarly to the IPA-assisted pure MAPbBr₃ composition (Subsec. 5.6.3), no scattering reflections were observed before the antisolvent drop. However, in the CsI-containing composition, no IPA-based structure was observed after antisolvent application. The IPA drop directly initiated cubic perovskite formation, without any intermediate structures. This seems to be an effect of 5% CsI addition to MAPbBr₃ composition. The scattering intensity from the perovskite phase was increasing towards the end of the spinning scan, indicating solvent evaporation and perovskite phase crystallization (Fig. 5.40(d)). The cubic perovskite phase showed a preferred orientation at 53° and 0° (Fig. 5.41(b)), indicating a possible successful incorporation of CsI into the MAPbBr₃ perovskite network [262].

The annealing procedure initiated the crystallization process, reflected in the decrease of FWHM, similarly to the effect, observed in Subsec. 5.2.5. A remarkable influence of CsI addition to the MAPbBr₃ composition is preserving a preferred orientation within the annealed perovskite film. The combination of Br within the composition, and 5% of CsI provides a pronounced preferred orientation to perovskite, which describes the difference between organic cation and mixed organic-inorganic cation compositions, such as FA:MA and FA:MA:Cs (compare Fig. 5.31(f) and Fig. 5.32(f)).

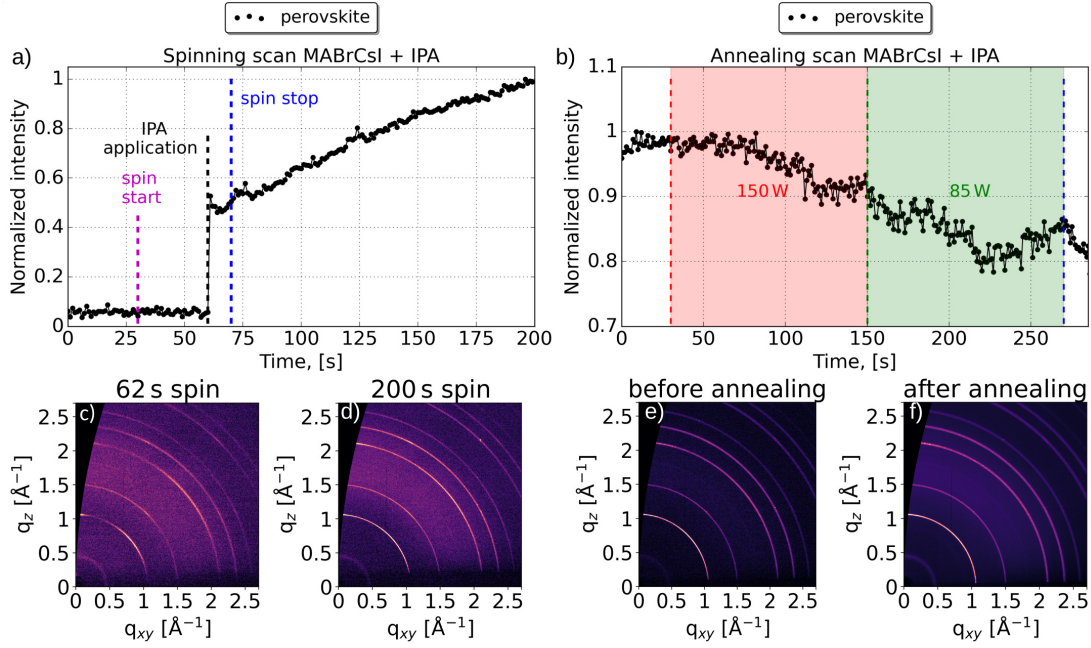


Figure 5.40.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) antisolvent-assisted spin-coating and (b) annealing steps of MAPbBr₃ + CsI perovskite thin film fabrication. Annealing was done for 120 s at 150 W and 120 s at 85 W. Exemplary GIWAXS scans (c), (d) after IPA application, (e) before and (f) after annealing.

5.7.7. Summary on the effects of 5% CsI incorporation and IPA antisolvent application on single cation compositions.

A direct comparison between single cation compositions with 5% CsI incorporated grown with the OSC method and IPA antisolvent-assisted deposition is presented in Fig. 5.41. For all antisolvent-assisted samples a better coverage in comparison to the OSC samples was observed, the incorporation of 5% CsI resulted in the appearance of a preferred orientation within the perovskite phase. This finding might hinder an essential difference of IPA antisolvent application and CsI incorporation effects on FA:MA and FA:MA:Cs composition, discussed in Subsec. 5.6.7, and suggest a unique role of Cs within the mixed cation composition, since the FAI·PbI₂-x·DMSO templating structure influences the whole mixed perovskite phase orientation within the final film [38].

5.8. Gas quenching-assisted perovskite crystallization

The following section is dedicated to the samples prepared by nitrogen jet-assisted method which are compared to the IPA antisolvent-assisted method. The introduction of the gas quenching method is provided in Subsec. 2.3.5 and is displayed in Fig. 2.19. Briefly,

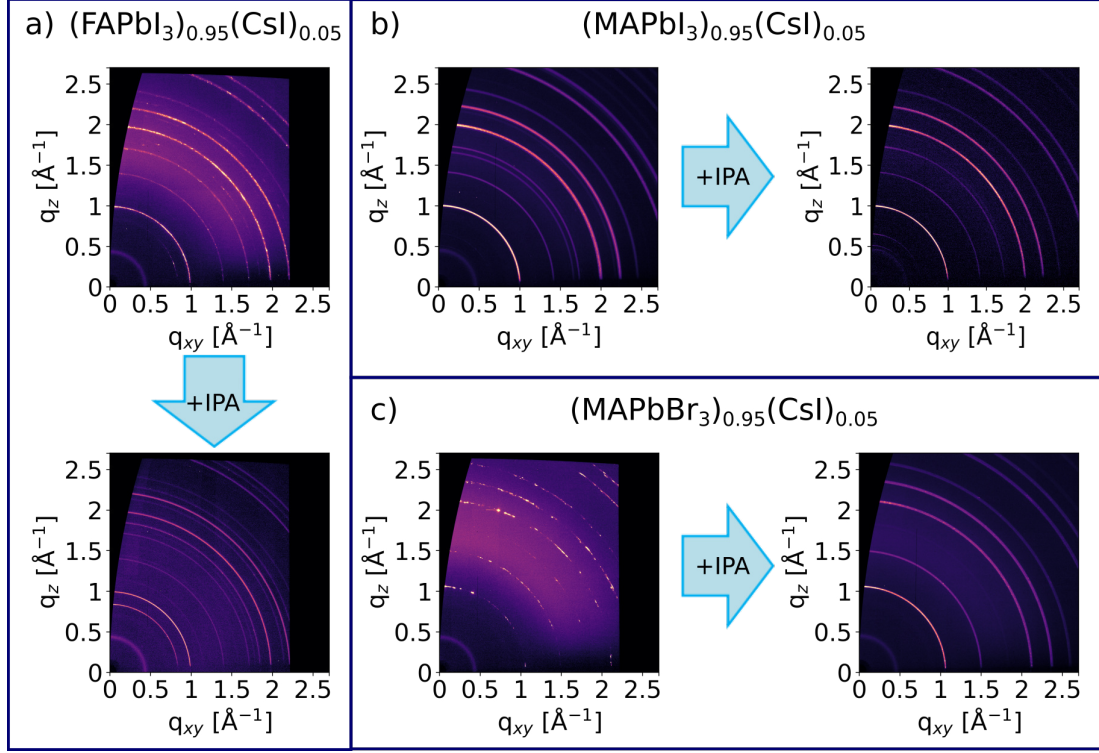


Figure 5.41.: Schematic summary of IPA antisolvent application on single cation compositions with an addition of 5% CsI: (a) FAPbI₃, (b) MAPbI₃ and (c) MAPbBr₃. IPA application improves thin film coverage and provides a preferred orientation to the perovskite phase.

Table 5.8.: Structural composition of the studied samples and solvents.

Sample	Solvent	Substrate
MAPbI ₃	DMF:DMSO (4:1)	Glass/ITO
FAPbI ₃	DMF:DMSO (4:1)	Glass/ITO
FA:MA	DMF:DMSO (4:1)	Glass/ITO
FA:MA:Cs	DMF:DMSO (4:1)	Glass/ITO

nitrogen gas stream saturates a deposited thin film, which leads to a rapid crystallization. All compositions were dissolved in a DMF:DMSO (4:1) solvent mixture. In order to achieve a higher scattering signal, thin films were deposited onto an ITO-coated glass substrate by spin-coating at 3000 rpm for 150 s, the nitrogen stream was switched on 15 s after the start of spinning for 135 s. The coated films were subsequently annealed by a halogen lamp. Both steps, spinning and annealing, were tracked by *in situ* GIWAXS at an angle of incidence $\alpha_i = 0.5^\circ$.

5.8.1. Methylammonium lead iodide

In the past research, MAPbI₃ composition dissolved in DMSO was studied by GIWAXS during gas quenching, it was found that the perovskite phase was formed *via* the intermedi-

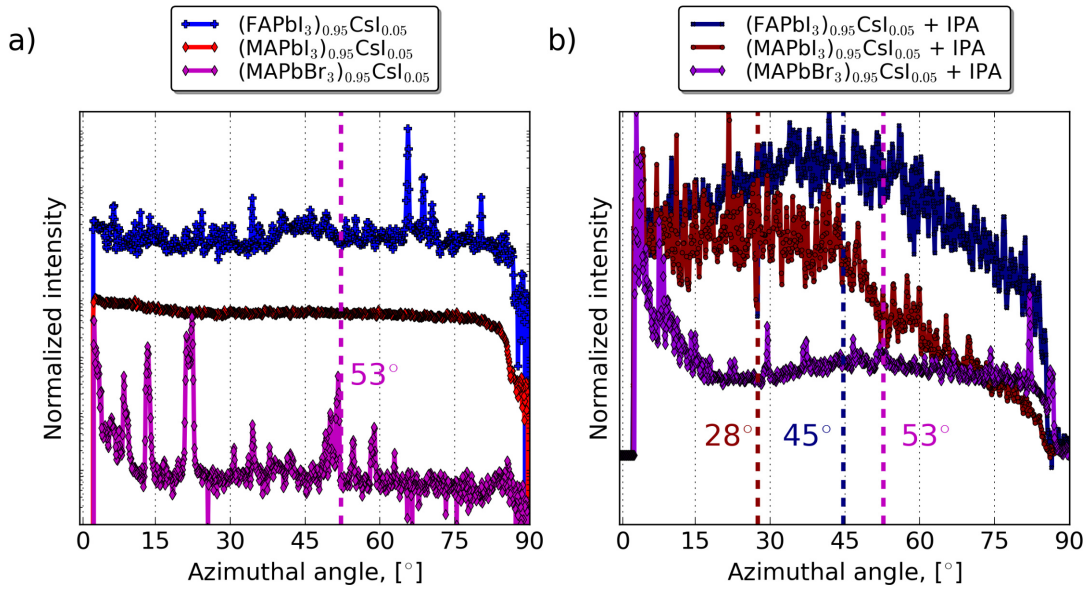


Figure 5.42.: Degree of orientation for perovskite phase in single cation samples FAPbI_3 , MAPbI_3 and MAPbBr_3 with 5% CsI deposited on bare glass substrates by: (a) OSC method and (b) IPA antisolvent-assisted method, 0° corresponds to the vertical orientation of the perovskite phase. The addition of 5% CsI to MAPbI_3 and FAPbI_3 improve thin film coverage and give preferred orientation, IPA application changes the angle of the preferred orientation. The addition of 5% CsI to MAPbBr_3 composition and IPA application results in better thin film coverage and the appearance of a preferred orientation of the perovskite phase at 0° .

ate phase $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ [15]. The GIWAXS scattering intensity evolution during gas quenching-assisted spin-coating procedure in Fig. 5.43(a) suggested, that around 10 s after switching on nitrogen stream, the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ intermediate phase was formed, the same as in IPA-assisted sample (Subsec. 5.6.1). The scattering intensity from this intermediate phase approached its maximum almost immediately and remained constant until the end of the spinning scan, indicating rapid crystallization due to the solvent evaporation. This result suggests higher connectivity of DMSO with MAI, in comparison to DMF solvent. It is more probable to create a DMSO-based solvent-based complex even if the solvent mixture contains only 20% of DMSO and 80% in the mixture is DMF. On the other hand, FA^+ cation is tending to create DMF-based intermediate phases in DMF-rich solutions. This is another fundamental difference between the studied big organic cations, MA^+ and FA^+ .

The annealing treatment at 150 W initiated partial solvent evaporation, leading to the slight increase of DMSO-based intermediate scattering intensity (Fig. 5.43(b)), weaker than in the case of an IPA antisolvent-assisted method (Fig. 5.24(b)). After 25 s of annealing, the DMSO-based solvent complex started its rapid conversion into the desired perovskite phase. The conversion profile of the intermediate phase was quite similar to

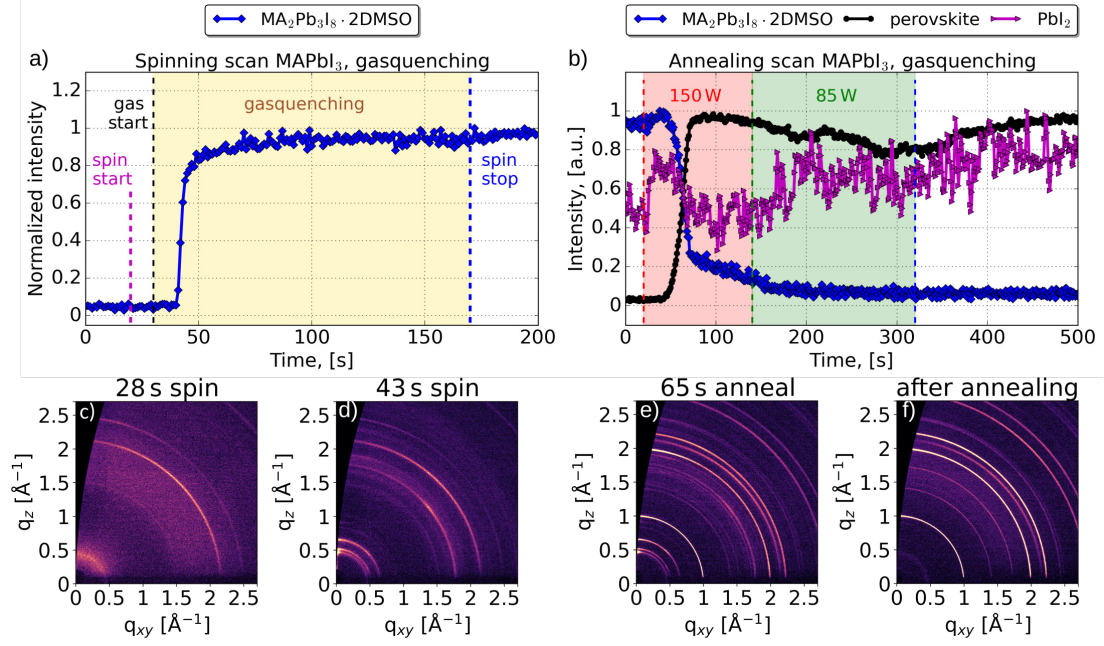


Figure 5.43.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) gas quenching-assisted spin-coating and (b) annealing steps of MAPbI₃ perovskite thin film fabrication. Annealing was done for 120 s at 150 W and 180 s at 85 W. Exemplary GIWAXS scans (c) before and (d) after nitrogen stream was switched on, (e) during and (f) after annealing.

that of the antisolvent-assisted sample, the intensity showed a two-step intensity decrease. This suggests a similar effect of antisolvent application and gas quenching: the fast conversion arises from the material, located closer to the surface and depleted by the halogen lamp, while the bulk of the thin film converts later due to the presence of some residual solvent. After 130 s of the annealing treatment, ~90% of the scattering intensity from the intermediate phase was gone. Later, a tiny amount of PbI₂ was formed as a result of the slight overheating (Fig. 5.43(f)). Its scattering intensity is quite noisy due to the low amplitude of the signal, indicating the low contents of the phase. The resulting perovskite phase had two preferred orientations, at 0° (vertical orientation) and at 45°, as displayed in Fig. 5.48(a). It happens possibly to the formation *via* the DMSO-based intermediate phase, which adapts preferred orientation under nitrogen stream, and transfers it to the perovskite phase, since it can serve as nucleation centers to form MAPbI₃ perovskite phase.

5.8.2. Formamidinium lead iodide

The FAPbI₃ composition was deposited by gas quenching-assisted method, the scattering intensity evolution of different phases during spin-coating procedure is displayed in Fig. 5.44(a). Similarly to the case of an IPA (Fig. 5.25(a)) and chlorobenzene [116] antisolvent-assisted methods, an additional treatment during spinning by nitrogen stream

initiated solvent evaporation, resulting in 2H hexagonal phase formation, which approached its scattering intensity maximum within 50 s and remained constant until the end of the spinning scan. Similarly to the antisolvent-assisted deposition, nitrogen jet provided preferred orientation to the formed hexagonal phase at 60° and 0° (Fig. 5.44(d)).

The annealing treatment initiated only slight solvent evaporation leading to small

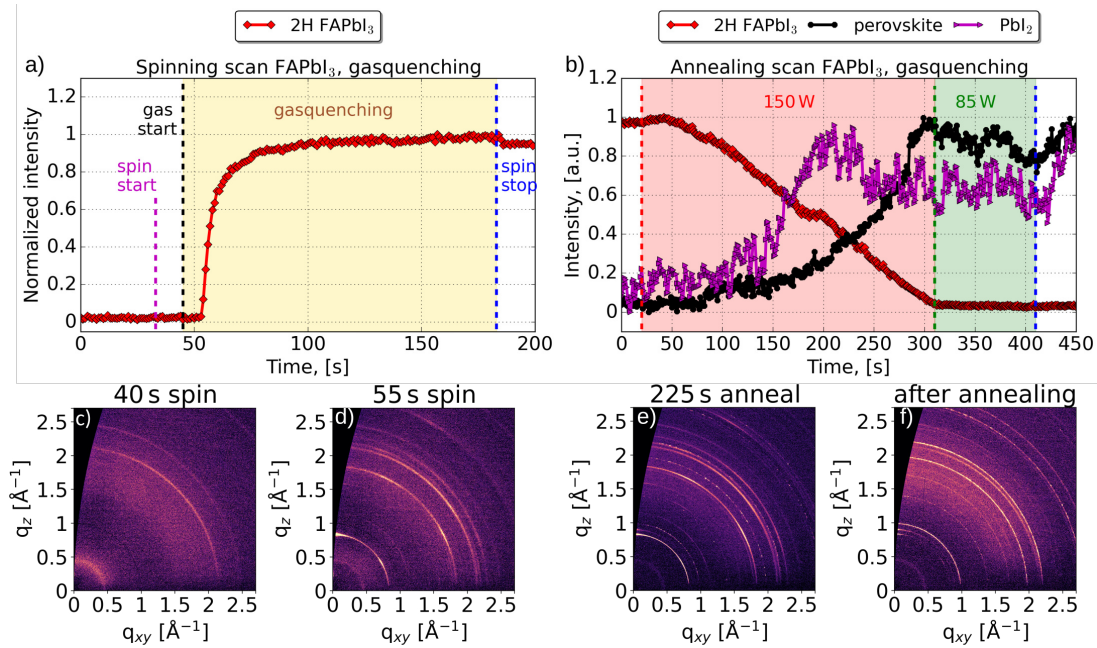


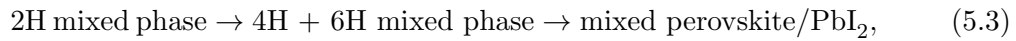
Figure 5.44.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) gas quenching-assisted spin-coating and (b) annealing steps of FAPbI₃ perovskite thin film fabrication. Annealing was done for 290 s at 150 W and 100 s at 85 W. Exemplary GIWAXS scans (c) before and (d) after nitrogen stream was switched on, (e) during and (f) after annealing.

increase of hexagonal phase scattering intensity (Fig. 5.44(b)), followed by its slow conversion into the perovskite phase within ~ 270 s of annealing at 150 W. Besides perovskite phase, a formation of a tiny amount of PbI₂ was detected towards the end of the annealing treatment (Fig. 5.44(f)). The resulting thin film had a good coverage, which is a positive influence of the gas quenching method in comparison to OSC method. Nevertheless, 2H hexagonal phase during annealing treatment did not transfer its preferred orientation to the cubic perovskite phase, which showed random orientation in the final film (Fig. 5.48(a)). This might have happened due to the conversion of one solid phase (hexagonal) into another solid phase (cubic), which does not preserve preferred orientation. This is another remarkable difference between the two most common organic cations for perovskite solar cells: unlike FA⁺, MA⁺ is capable of forming a perovskite phase with preferred orientation, delivered by the DMSO-based intermediate phase.

5.8.3. Double cation sample FA:MA

After studying the effects of nitrogen gas jet on the crystallization pathways of the most common iodide-based single cation compositions, an effect of gas quenching treatment during spin-coating and annealing on a mixed cation and mixed halide FA:MA composition was studied. After ~ 15 s of the nitrogen stream treatment, presumably a combination of the 2H and 4H mixed hexagonal polytypes [71] was formed (Fig. 5.45(a)), similarly to the IPA antisolvent-assisted method (Fig. 5.31(a)). Besides that, a small amount of the 6H mixed hexagonal phase [71], characterized by the scattering reflection at $0.86 \text{ \AA}^{-1}$, was formed. The scattering intensities from all hexagonal phases reached their maxima after 20 s of nitrogen gas jet treatment and started their partial conversion into the mixed perovskite phase until the end of the spinning scan. The perovskite phase formation was not observed for this composition, deposited by OSC or antisolvent-assisted method, which indicates a potentially positive influence of the gas quenching method on the FA:MA composition crystallization. Another remarkable difference arises from the absence of both DMF- and DMSO-based intermediate phases, which appeared in both OSC method (Fig. 5.11(a)) and IPA-assisted method (Fig. 5.31(a)).

The annealing treatment presumably initiated the following conversion sequence:



which is similar to the previous research [71], with the main difference being the absence of the DMSO-based intermediate phase. The partial conversion of hexagonal polytypes into mixed perovskite phase was finished within 180 s of annealing at 150 W, which is the same as in the sample grown by one-step method (Fig. 5.21(b)). Alongside with positive dynamics of hexagonal-to-cubic conversion, a tiny amount of PbI_2 was formed within the sample due to over annealing.

5.8.4. Triple cation sample FA:MA:Cs

The studied FA:MA:Cs composition is similar to the FA:MA:Cs:Rb composition, produced by gas quenching method, which demonstrated high average energy conversion efficiency in perovskite solar cells, around 19.7% [119]. Similarly to the previously studied FA:MA composition, nitrogen jet partially evaporated solvents within coated film and after 10 s induced crystallization, which led to rapid formation (15 s) of the 4H phase and slightly delayed (6 s) perovskite phase growth (Fig. 5.46). The perovskite phase was growing slower, its scattering intensity was higher than in the case of FA:MA composition. This is an indication of the perovskite phase stabilization, resulting in more content within coated film before annealing treatment. The absence of the $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ intermediate phase [152], which was observed during OSC and antisolvent-assisted methods, indicates the influence of gas quenching treatment. The 4H hexagonal phase was slowly converting

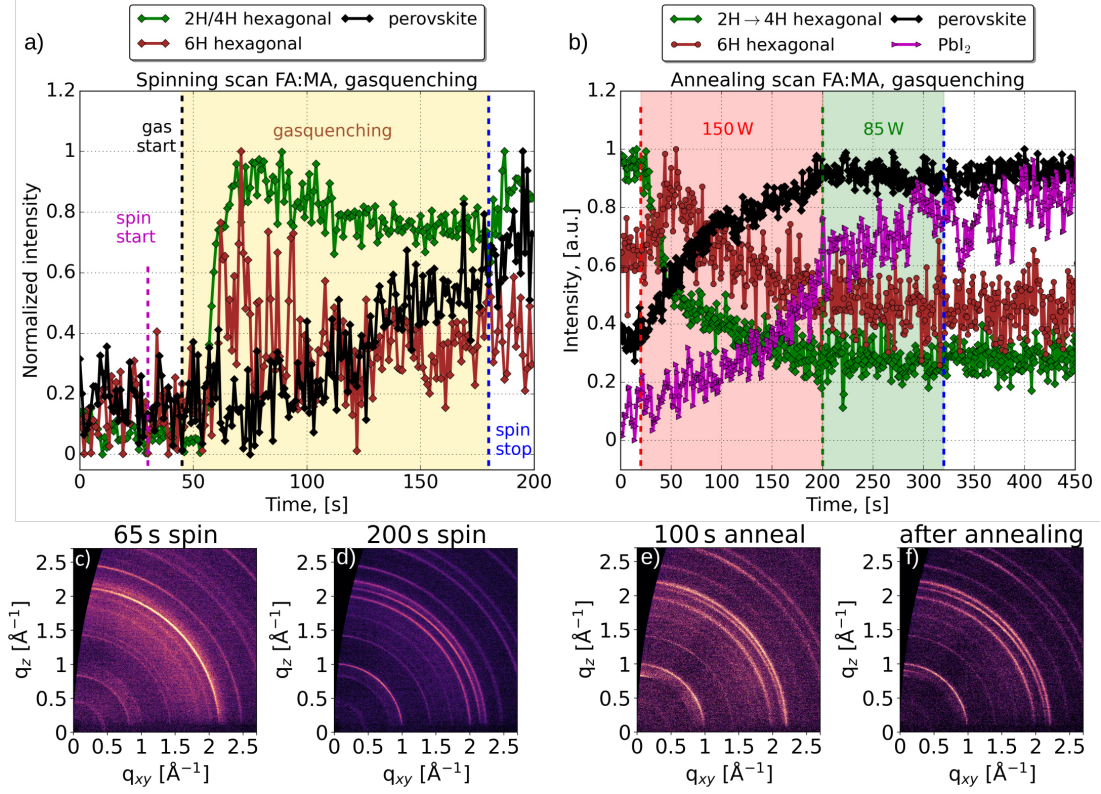


Figure 5.45.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) gas quenching-assisted spin-coating and (b) annealing steps of FA:MA perovskite thin film fabrication. Annealing was done for 180 s at 150 W and 120 s at 85 W. Exemplary GIWAXS scans during (c), (d) nitrogen-assisted spin-coating, (e) during and (f) after annealing.

into cubic perovskite phase until the end of the spinning scan.

Before annealing, a major amount of the mixed perovskite phase was formed ($\sim 70\%$ of maximum), which further indicates perovskite phase stabilization as a consequence of adding Cs cation into double cation composition. The annealing treatment initiated further conversion of 4H mixed hexagonal phase into perovskite phase (Fig. 5.46(b)). The final film showed the presence of perovskite phase and a tiny fraction of 4H hexagonal polymorph (Fig. 5.46(f)). The resulting perovskite phase exhibited a preferred orientation at 45° , which is similar to the orientation of both DMSO-based intermediate and perovskite phases within the pure MAPbI_3 composition, grown by gas quenching method (Fig. 5.48). The resulting orientation in FA:MA:Cs can be explained by the formation of mixed perovskite phase based on MAPbI_3 crystallites, which adapted the preferred orientation directly under exposure to the nitrogen flow and avoided crystallization from the DMSO-rich phase which creates nucleation centers to form perovskite phase [254].

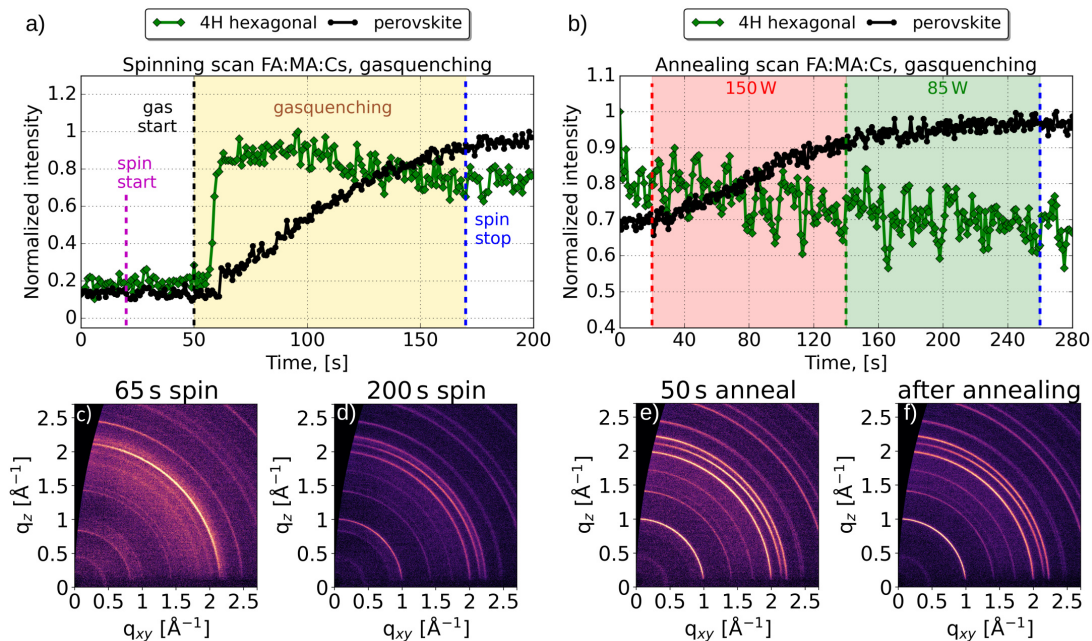


Figure 5.46.: Scattering intensity evolution of the structures extracted from *in situ* GIWAXS during (a) gas quenching-assisted spin-coating and (b) annealing steps of FA:MA:Cs perovskite thin film fabrication. Annealing was done for 120 s at 150 W and 120 s at 85 W. Exemplary GIWAXS scans (c), (d) during the nitrogen stream, (e) during and (f) after annealing.

5.8.5. Summary on the effects of gas quenching treatment

The goal of using nitrogen flow during spin-coating was to induce solvent evaporation, resulting in supersaturation within the thin film and faster crystallization than in the case of one-step method. A brief summary on crystallization sequence for gas quenching-assisted samples is displayed in Fig. 5.47. The effect of gas quenching on single cation compositions was similar to that of the IPA antisolvent application: during spin-coating of MAPbI₃ composition the formation of (MA)₂Pb₃I₈·2DMSO solvent-based complex was observed, while for FAPbI₃ composition, nitrogen flow induced the formation of 2H hexagonal FAPbI₃ phase.

For the mixed cation compositions, nitrogen flow strongly changed the crystallization pathway, which is reflected in suppressing the formation of solvent-based intermediate phases, unlike for antisolvent-assisted growth. For example, the FA:MA composition showed the formation of 2H/4H, 6H hexagonal polymorphs and cubic perovskite, the latter one was not observed in the case of IPA antisolvent application prior to annealing, which suggests that gas quenching is better in stabilization of perovskite phase. Nevertheless, the conversion sequence was similar to that of OSC and antisolvent-assisted method, excluding solvent-based intermediates. For the FA:MA:Cs sample, 4H and cubic perovskite phase were formed during spin-coating, similarly to IPA antisolvent-assisted sample, hexagonal-to-cubic conversion took place during thin film deposition before an-

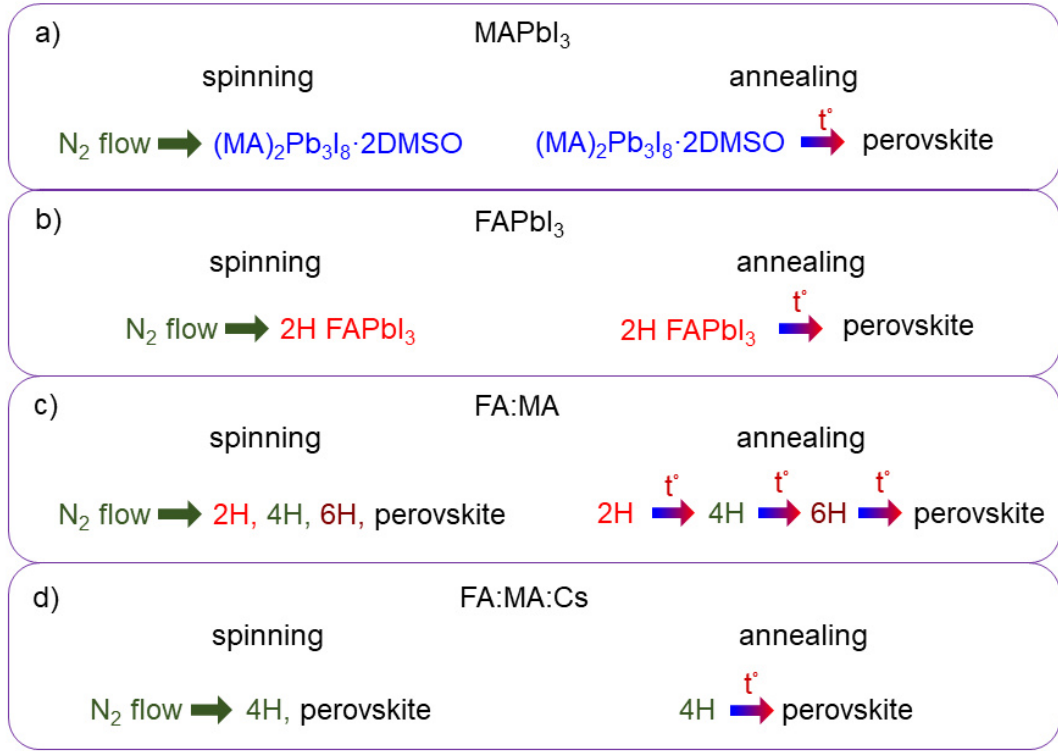


Figure 5.47.: Crystallization sequence extracted from *in situ* GIWAXS measurements during spinning (left column, green arrows) and annealing (right column, gradient arrows with t^0 meaning heating) of: (a) MAPbI₃; (b) FAPbI₃; (c) FA:MA and (d) FA:MA:Cs compositions grown by gas quenching method. Single cation compositions show kinetics similar to IPA antisolvent-assisted growth, while nitrogen flow suppressed the formation of solvent-based intermediate phases in mixed cation compositions

nealing. The annealing procedure induced partial conversion of tiny residuals of 4H mixed hexagonal phase into perovskite phase.

The orientation profiles of (100) perovskite phase reflection within the single cation compositions, deposited by gas quenching method, extracted from *ex situ* GIWAXS patterns, are displayed in Fig. 5.48(a). For the MAPbI₃ composition two distinct peaks reflecting preferred orientation were observed: 45° and 0°, while FAPbI₃ perovskite phase was randomly oriented. Such a difference originates from crystallization under nitrogen flow: for MA-based composition, DMSO-based intermediate phase adapted two preferred orientations with reflections at 45° and 0° and transferred both of them to cubic perovskite. For the FAPbI₃, 2H FAPbI₃ phase received preferred orientation at 60° and 0°, while annealing treatment initiated conversion of the solid hexagonal phase into the solid perovskite phase without preferred orientation transfer, similarly to antisolvent-assisted method, displayed in Fig. 5.30.

The orientation profiles of (100) perovskite phase reflection within the mixed cation gas

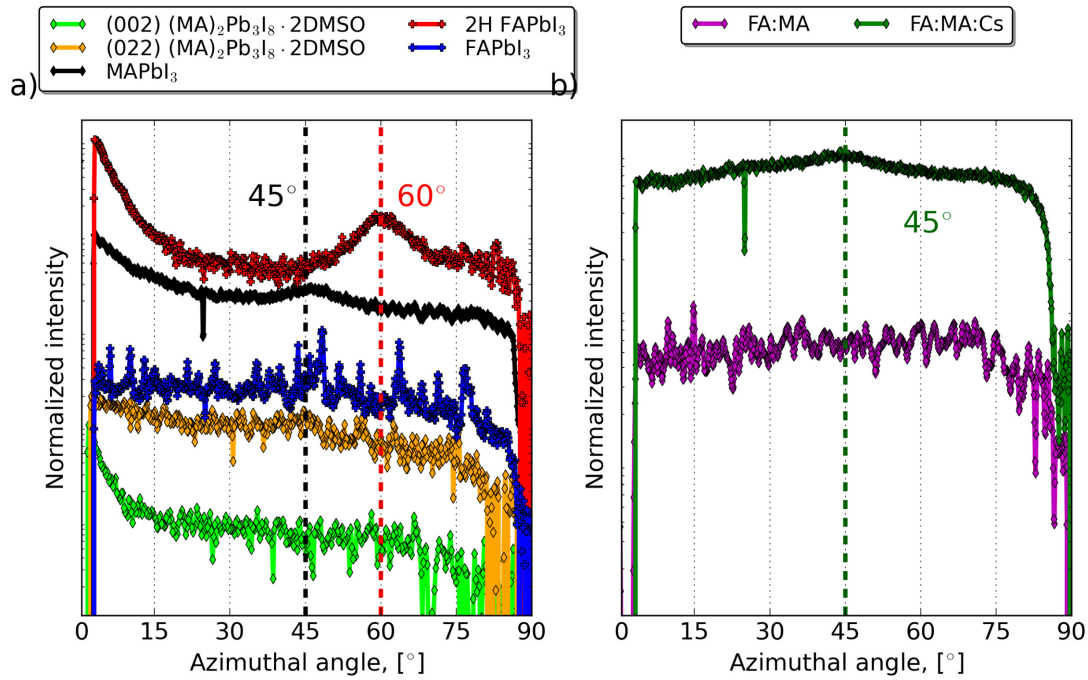


Figure 5.48.: Orientation profiles of the DMSO-based intermediate and perovskite phases extracted from *ex situ* GIWAXS after annealing of: (a) FAPbI₃ and MAPbI₃; (b) FA:MA and FA:MA:Cs compositions grown by gas quenching method, 0° corresponds to the vertical orientation of the perovskite phase.

quenching-assisted samples, extracted from *ex situ* GIWAXS patterns, are displayed in Fig. 5.48(b). Cubic perovskite within the FA:MA composition was randomly oriented, which can be a consequence of the complex formation sequence, involving three mixed hexagonal polytypes. Since hexagonal phases exhibit a preferred orientation under nitrogen flow, they transform into randomly oriented mixed perovskite upon annealing, as in the case of the 2H phase transformation in the FAPbI₃ composition. The addition of 5% CsI, as expected, qualitatively changes the conversion sequence by suppressing the formation of 2H and 6H hexagonal phases, thus making mixed perovskite phase more energetically favorable. The perovskite phase under gas quenching-assisted deposition adapts preferred orientation at 45°, similarly to one of the preferred orientations, observed for MAPbI₃ composition, which might suggest its origin.

5.9. Conclusions from this chapter

This chapter unravels the complexity of crystallization pathways of 3D perovskites depending on composition and preparation method. It starts with thin films deposited by one-step method tracked only during hotplate annealing; the compositions studied included one to four cations and one to two halides. Then, the first tests of the spin-coating

chamber are described, focusing on the growth of 3D perovskite structures using OSC, solvent assisted deposition, and gas quenching, the results are summarized in Fig. 5.1 (single cation compositions) and Fig. 5.2 (mixed cation compositions).

Single cation compositions, based on iodide, formed solvent based intermediate phases: $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ within MAPbI_3 and $\text{FAPbI}_3 \cdot \text{DMF}$ within FAPbI_3 composition, respectively, and required an annealing treatment in order to achieve the target perovskite phase. The bromide-based MAPbBr_3 composition directly formed cubic perovskite phase, while annealing treatment induced the increase in size of the coherently scattering domains. CsPbI_3 composition was not converted into cubic perovskite, while it still showed an interesting feature upon annealing - a two-step increase of the scattering intensity from the orthorhombic CsPbI_3 phase, which might reflect the formation of Cs-based phases within thin film prior to annealing. The same trend was observed for the mixed perovskite phase in mixed cation compositions with Cs incorporated, such as FA:MA:Cs and FA:MA:Cs:Rb , and it was found that the duration of the first crystallization step was decreasing with the decreasing amount of Cs included in the structure.

The mixed cation mixed halide composition FA:MA showed the formation of both DMF- and DMSO-based intermediate phases, which converted into other phases upon annealing. The DMF-based structure has transformed into 2H FAPbI_3 phase, which then, combined with the DMSO-based intermediate phase, converted into 4H mixed hexagonal phase, followed by its transformation into mixed 6H and perovskite phases. The 4H hexagonal phase was found to be an important intermediate phase between the precursor phases and the target perovskite phase, which might be caused by its low formation energy due to the high bromide content, predicted by DFT [227]. The compositions with three and four cations, FA:MA with incorporated 5% Cs^+ and 5% $\text{Cs}^+ + 5\% \text{Rb}^+$, respectively, exhibited perovskite phase formation prior to annealing, which is a positive sign of cation mixing, resulting in perovskite phase stabilization [138]. As the number of cations increases, the coherent scattering domain sizes of the perovskite phase and its phase fraction within the thin film also increase, leading to the purest perovskite phase for the quadruple cation composition FA:MA:Rb:Cs .

The additional research, focused on FAPbI_3 composition, dissolved in DMF, showed the formation of $\text{FAPbI}_3 \cdot \text{DMF}$ phase as a metastable state between the $\text{FAPbI}_3 \cdot 4\text{DMF}$ and $\text{FAPbI}_3 \cdot 2\text{DMF}$ solvent-based intermediate phases and 2H FAPbI_3 phase, which is converted into cubic perovskite phase upon annealing. The $\text{FAPbI}_3 \cdot \text{DMF}$ phase was previously obtained artificially [148] from $\text{FAPbI}_3 \cdot 2\text{DMF}$ by toluene washing and vacuum drying, while in another source it was claimed that, unlike $\text{MAPbI}_3 \cdot \text{DMF}$ [98], it can not be formed at all [147]. The ability of measuring *in situ* GIWAXS during thin film crystallization allowed to gain an essential insight into DMF-based intermediate phases.

The single cation compositions were dissolved in a (4:1) DMF:DMSO solvent mixture, but this did not drastically affect the results compared to the OSC data set, which was studied only during the annealing step. The major difference originates from the appear-

ance of the preferred orientation in MA-based compositions, since it could be obtained during spin-coating by either solvent-based intermediate phase (iodide-based composition) or directly by the cubic perovskite phase (bromide-based composition). On the other hand, cubic perovskite phase in FAPbI₃ composition did not obtain any preferred orientation, since during spin-coating mainly solid 2H FAPbI₃ phase was formed, and upon annealing it did not transfer the preferred orientation. The FAI:PbI₂-x·DMSO templating structure, observed previously during the fabrication of triple cation composition by antisolvent-assisted method [38], was also identified during spin-coating of the FAPbI₃ composition. However, since only solvent-free hexagonal phase was formed, it did not form the preferred orientation, but still improved thin film coverage. Both methods, antisolvent-assisted deposition and gas quenching, induce supersaturation of the deposited thin film and result in rapid crystallization.

For the multi-cation compositions, a similar trend to the previously discussed samples was observed. In particular, the FA:MA composition exhibited a convenient crystallization pathway previously reported [71], namely 2H→4H→6H→mixed perovskite phases for different fabrication methods. In addition, for the IPA antisolvent-assisted method, three solvent-based intermediate phases were formed, two DMSO-based (FAI: PbI₂-x·DMSO templating structure [38] and (MA)₂Pb₃I₈·2DMSO [152]) and one DMF based (similar to FAPbI₃·DMF [148]), which have also been transformed into hexagonal and mixed perovskite phases. The latter adopted a preferred orientation at 0° and 53°, presumably from the perovskite seeds based on (MAPbBr₃)_{0.95}CsI_{0.05} formed prior to annealing, and the MAPbI₃-rich fraction converted from the DMSO-based intermediate phase. The FA:MA:Cs composition exhibited perovskite phase formation immediately after IPA antisolvent application, similar to the previously reported triple cation composition [38]. The preferred orientation of the perovskite phase was presumably obtained *via* the FAI:PbI₂-x·DMSO templating structure induced by IPA antisolvent application. Since the triple cation composition stabilizes the perovskite phase, the preferred orientation obtained during the spin-coating process is maintained even after thermal annealing.

The addition of 5% CsI to single cation compositions improves the thin film coverage already for the OSC method and enhances the preferred orientation of the perovskite phase. The use of IPA antisolvent resulted in even better coverage with much more pronounced preferred orientation, which appears to be more beneficial for perovskite phase stabilization.

Gas quenching assisted growth of perovskite compositions further improved the thin film coverage compared to the OSC method. Nitrogen gas quenching deposition induced the preferred orientation of the perovskite phase in MAPbI₃ and FA:MA:Cs compositions. The MAPbI₃ composition showed two maxima, at 0° and 45°, which could be induced by the transformation of the DMSO-based intermediate phase, while the triple cation composition showed a preferred orientation of the perovskite phase only at 45°, which could be caused by the high fraction of FAPbI₃ in the mixture.

6. 2D perovskite crystallization data

6.1. Introduction

The previous chapter showed growth kinetics of different 3D perovskite compositions. The goals of this chapter are to resolve the complexity of crystallization pathways for 2D perovskite compositions during spin coating/annealing steps using developed spin-coater and study the influence of different spacer cations/small cations/halides on the growth kinetics and phase distribution. The various critical challenges, which are faced by three dimensional perovskites, such as their tendency to degrade under heat [263, 264] and moisture [265–267] due to the environmental vulnerability of small cations (such as MA^+ and FA^+), can be partially solved by developing layered hybrid perovskites. Using slightly larger organic molecules results in forming layered structures which, due to their reduced volatility and greater hydrophobicity, increase environmental stability of the materials [268–270]. As it was introduced earlier, there are two types of 2D perovskite structures, RP and DJ, depending on the spacer cation: monofunctional or bifunctional, respectively (Fig. 3.7). The results of this chapter spot the difference for RP BNA-based perovskites between the crystallization pathways depending on target composition (target dimensionality, $\tilde{n} = 1\text{--}3$), small cations within the composition (MA^+ or FA^+) and halides (I^- or Br^-). Besides that, some of $n = 1$ DJ compositions, based on PDMA and PDEA were studied and the influence of annealing profile on the resulting 2D phase orientation was observed.

6.2. BNA- and iodide-based perovskites

BNA spacer cation, which was introduced in Sec. 3.3, is one of the common components for producing 2D perovskites due to its exceptional properties. Various compositions, based on BNA and iodide with target dimensionalities of $\tilde{n} = 1\text{--}3$, were studied previously only by *ex situ* GIWAXS [176], while current section reveals the complexity of their crystallization kinetics by using *in situ* GIWAXS during spin-coating and annealing. The experimental details of BNA-based thin film fabrication are presented below, in Sec. 6.2.1. Additional insights, captured by X-rays, reveal the complexity of the mechanisms, caused by interaction of BNA and iodide within the deposited film, which is followed by studying the influence of halide substitution for bromide, discussed in Sec. 6.3.

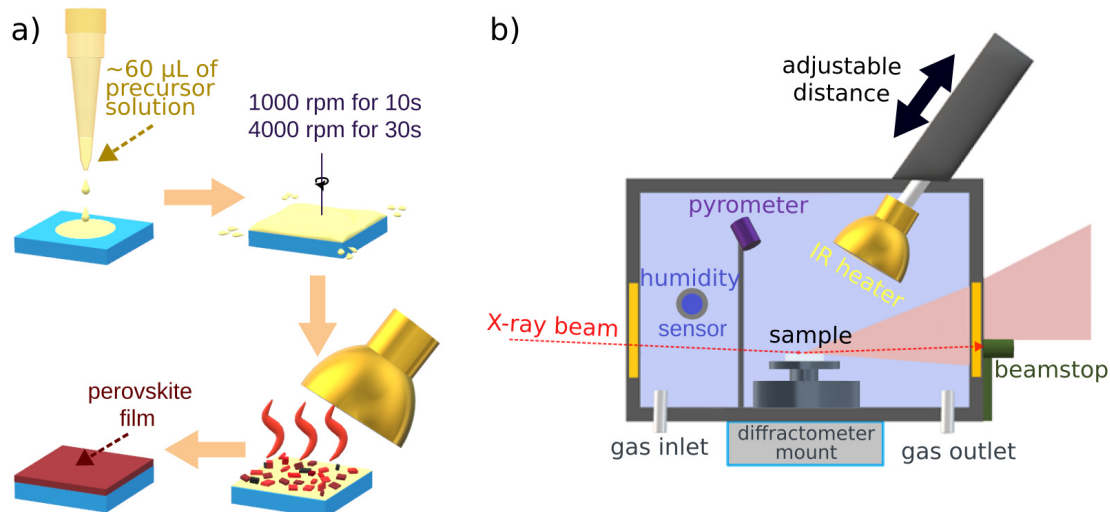


Figure 6.1.: (a) Step-by-step sample fabrication procedure of 2D perovskite samples and (b) experimental chamber used for *in situ* X-ray scattering experiments.

6.2.1. Experimental details

All studied compositions were deposited onto 1 mm thick 10×10 mm ITO-coated glass substrates. Substrate surface preparation included ultrasonic bath cleaning in IPA (5 min) and acetone (5 min). After that, substrates were plasma cleaned in argon plasma, as described in Subsec. 2.3.1. The clean substrates were fixed to a sample table in the spin-coating chamber with heat-resistant adhesive tape. After alignment, 60 μL of the corresponding precursor solution were applied on the substrate and spin-coated for 10 s at 1000 rpm and 30 s at 4000 rpm, as displayed in Fig. 6.1, following one-step deposition method. The annealing process was conducted using a halogen lamp positioned 40 mm from the sample (the closest position), and the surface temperature of the sample was estimated using a pyrometer. The annealing process was monitored by visual inspection of the scattered reflections from different phases.

6.2.2. Composition $\tilde{n} = 1$ $(\text{BNA})_2\text{PbI}_4$

To gain a comprehensive understanding of 2D perovskites based on BNA and iodide, this research will first focus on $(\text{BNA})_2\text{PbI}_4$, a 2D RP composition with a target dimensionality of $\tilde{n} = 1$. It was studied with two different annealing profiles: a short, 54 s temperature ramp up to 112°C, and a long, 115 s annealing at $\sim 83^\circ\text{C}$, to see the impact of annealing on crystallization pathways (Fig. 6.2(d)). A list of identified structures with their corresponding reference names, scattering reflection positions and lattice parameters is provided in Tab. 6.1. A comparison of the preferred orientation corresponding to the target $n = 1$ phase and multiple additional $n = 1$ polymorphs, as well as raw GIWAXS data, is displayed in Fig. 6.2(a-c). The deposited films had a slightly different amounts of the solvent, $(\text{BNA})_2\text{PbI}_{4-1}$ had more of the liquid phase within the film due to the presence of the

Table 6.1.: Lattice parameters of the BNA lead iodide $n = 1$ polymorphs in sample 1, observed during crystallization process.

Structure	Reflection, $\text{\AA}^{-1}$	a , $\text{\AA}$	b , $\text{\AA}$	c , $\text{\AA}$
poly_1	0.43	6.36	7.06	29.2
poly_2	0.44	22.61	18.09	28.55
Literature*	0.442	9.14	8.67	28.6
$n = 1$ phase	0.45	–	–	27.9
poly_3	0.47	8.51	8.16	26.7
poly_4	0.5	–	–	25

scattering signal at $|q| = 0.4 \text{ \AA}^{-1}$ (indicated with a white arrow), unlike the $(\text{BNA})_2\text{PbI}_4$ -2, which had partially solidified by the beginning of the annealing procedure, and induced the formation of the structure characterized by the reflection at $|q| = 0.52 \text{ \AA}^{-1}$ (indicated with an orange arrow) corresponding to one of the polymorphs, namely poly_3 (Tab. 6.1). Note that the c unit cell parameter in poly_2 is closer to the literature value [150], and is not called as $n = 1$ phase only due to the differences in a and b , since the fitting was done to the *in situ* GIWAXS data during crystallization. The initial condition of sample 2 (more solid state) and prolonged annealing treatment resulted in PbI_2 formation with its reflection at $|q| = 0.89 \text{ \AA}^{-1}$ (indicated with a yellow arrow), whereas for the sample 1, the scattering signal at $|q| = 0.9 \text{ \AA}^{-1}$ followed the same evolution trend as the Bragg peak at $|q| = 0.45 \text{ \AA}^{-1}$, indicating its origin from the $n = 1$ phase, but second order reflection. During the annealing procedure we could observe a complex interplay of different $n = 1$ polymorphs, which seems to be a feature for iodide-based RP compositions. Before the annealing has started, there was no scattering signal from crystalline phases due to the presence of precursor solvents which scattered the incoming X-ray beam, while the annealing treatment initiated the following crystallization sequence:

$$\text{poly}_1 \rightarrow \text{poly}_2 \rightarrow n = 1 \text{ phase} \rightarrow \text{poly}_3 \rightarrow \text{poly}_4 \quad (6.1)$$

This conversion corresponds to decreasing unit cell length which might be due to the solvent evaporation, resulting in more compact packing of 2D phases. The position and intensity jumps of the peak at $q_z = 0.47 \text{ \AA}^{-1}$ (poly_3), which was identified as an intermediate state of the phase in a form of BNA-based $n = 1$ polymorph in both deposited samples, it happened once the annealing was switched off, i.e. during sample cooling, which can be described as a relaxation of the strain within the deposited film. For the sample with rapid hot annealing (sample 1) this Bragg peak was sharper in time scale whereas for the sample with slow prolonged annealing (sample 2) it was present for longer times, possibly due to the influence of PbI_2 on the top of the sample, which limited flexibility of the BNA spacer cations within the phases or due to the lower temperature of the spacer cations. A partial conversion into poly_4 with its position at around $|q| = 0.5 \text{ \AA}^{-1}$ was observed: for the sample 1, poly_1 and poly_2 remained constant, whereas $n = 1$

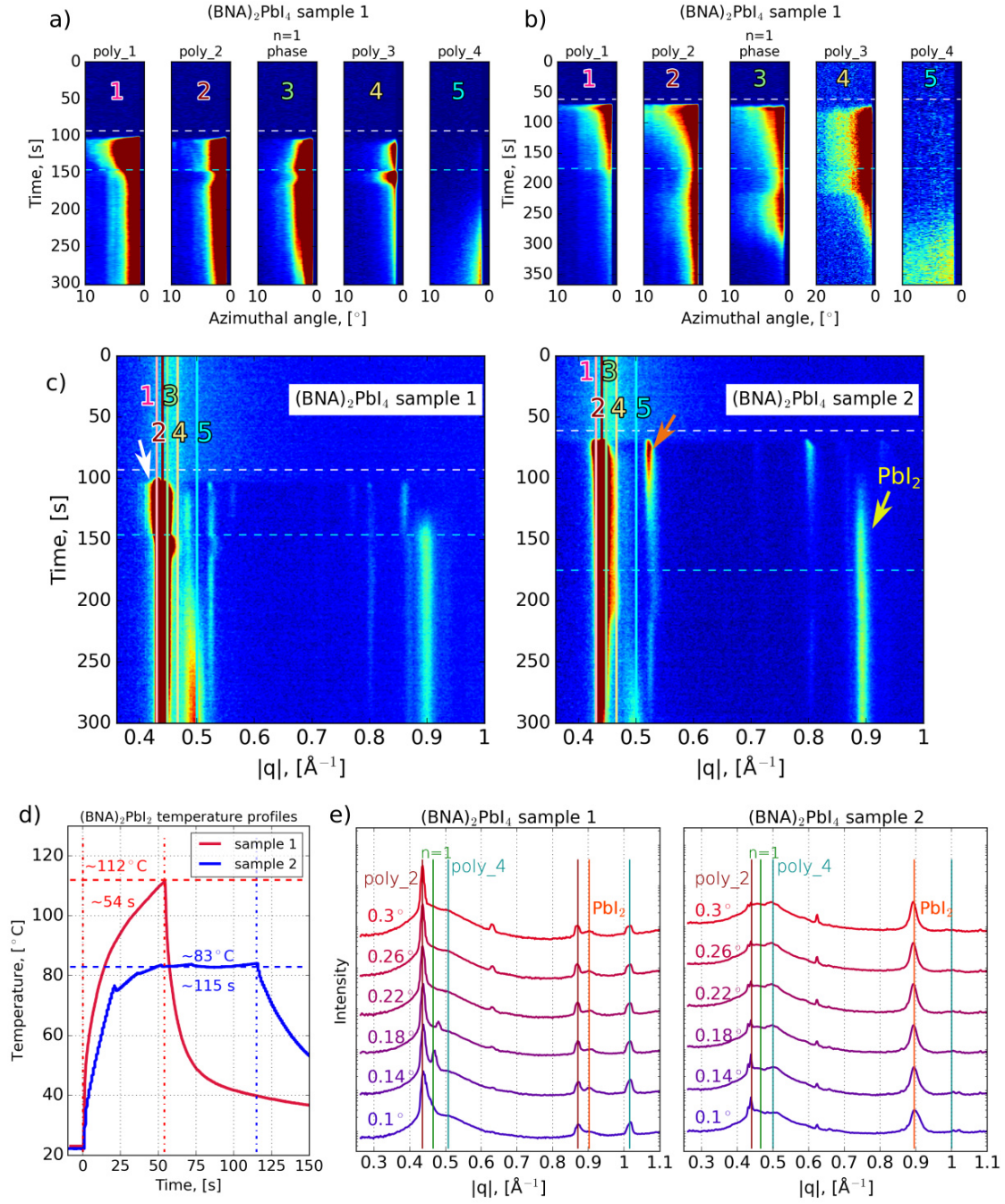


Figure 6.2.: Orientation profiles of $n = 1$ polymorphs and an $n = 1$ phase in $(\text{BNA})_2\text{PbI}_4$ composition, extracted from *in situ* GIWAXS during the annealing procedure: (a) sample 1 - rapid high T annealing and (b) sample 2 - slow low T annealing. Azimuthally integrated synchrotron-based GIWAXS patterns in waterfall plots, displaying the crystallization of c) sample 1 and d) sample 2. e) Annealing profiles for both samples: sample 1 was heated up to 112°C in 54 s, sample 2 was heated up to 83°C in 115 s. f) Integrated intensities of angular-dependent GIWAXS scans after annealing with marked structures in sample 1 (left) and sample 2 (right).

phase converted into poly_4; for sample 2 a reflection at $|q| = 0.44 \text{ \AA}^{-1}$ remained constant and other two, located at $|q| = 0.435 \text{ \AA}^{-1}$ and $0.452 \text{ \AA}^{-1}$, vanished. For both samples, preferred vertical orientation of the $n = 1$ phases and $n = 1$ polymorphs was observed, which suggests that this RP composition can be used a capping layer on top of the 3D perovskites to increase its environmental stability.

The GIWAXS data and integrated scattering intensities, acquired after annealing, are displayed in Fig. 6.3(a,b) and Fig. 6.2(e), respectively. Both samples showed the presence of two 2D structures: poly_2 and poly_4, the sample 2 additionally showed the presence of PbI_2 as a result of partial decomposition, which is supported by *in situ* GIWAXS measurements (Fig. 6.2(a,b)) and *ex situ* XRR measurements (Fig. 6.4 and Fig. 6.7). We assume that the growth with perpendicular orientation to the surface is more favorable for the $n = 1$ phase in BNAI-based $\tilde{n} = 1$ composition due to the annealing geometry and the nature of the BNA spacer cation. An extensive heating of BNA-based compositions might lead to the random orientation of the resulting $n = 1$ phase.

An interesting feature was observed additionally on the GIWAXS patterns with varying angles of incidence α_i : a refraction effect [271], resulting in doubling of the $n = 1$ phase reflections at angles of incidence between 0.12° and 0.2° , as displayed in Fig. C.2(a). This effect occurs when the surface condition of the final thin film is good, and is observed between the critical angles of the target BNA- and I-based 2D RP $n = 1$ phase (0.12°) and an ITO coating on the substrate (0.2°). The same feature was observed for BNA- and Br-based $\tilde{n} = 1$ compositions, which suggests that BNA spacer cation favors the formation of $n = 1$ thin films with good surface quality, which might be beneficial for applications as capping layers on 3D perovskite structures. A direct comparison of the GIWAXS data, collected in this work and literature [176] shows a clear improvement in understanding the nature of BNA in $\tilde{n} = 1$ target compositions. For instance, X-ray diffraction XRD data in the published research shows multiple scattering features without a clear explanation of their origin, while *ex situ* GIWAXS data shows a thermally degraded BNA-based sample which is characterized by the presence of the Bragg peak from a thermally degraded polymorph at $|q| = 0.5 \text{ \AA}^{-1}$ and a strong reflection from PbI_2 at $|q| = 0.89 \text{ \AA}^{-1}$.

An additional comparison was done for the studied $(\text{BNA})_2\text{PbI}_4$ composition: a sample with rapid conversion (sample 1) was compared to an *ex situ* sample, produced by A. Dučinskas, with the same composition of $(\text{BNA})_2\text{PbI}_4$, dissolved in DMF solvent, and annealed at 100°C for 10 min. The initial sample was probed by XRD, then it was exposed to 90°C for 5 days in argon atmosphere, which led to the partial decomposition of the 2D phase. The resulting degraded sample was probed by XRD and compared to the *in situ* GIWAXS measurements during thin film fabrication, as displayed in Fig. C.3. The pristine sample, annealed by a hotplate, displayed the presence of scattering signals originating from poly_1 and poly_2. The XRD of the degraded sample indicated the appearance of the poly_3, which is characterized by the reflection at $\sim 0.495 \text{ \AA}^{-1}$. Comparison of the *in situ* and *ex situ* samples lead to the following conclusion: the poly_2 phase tends to convert

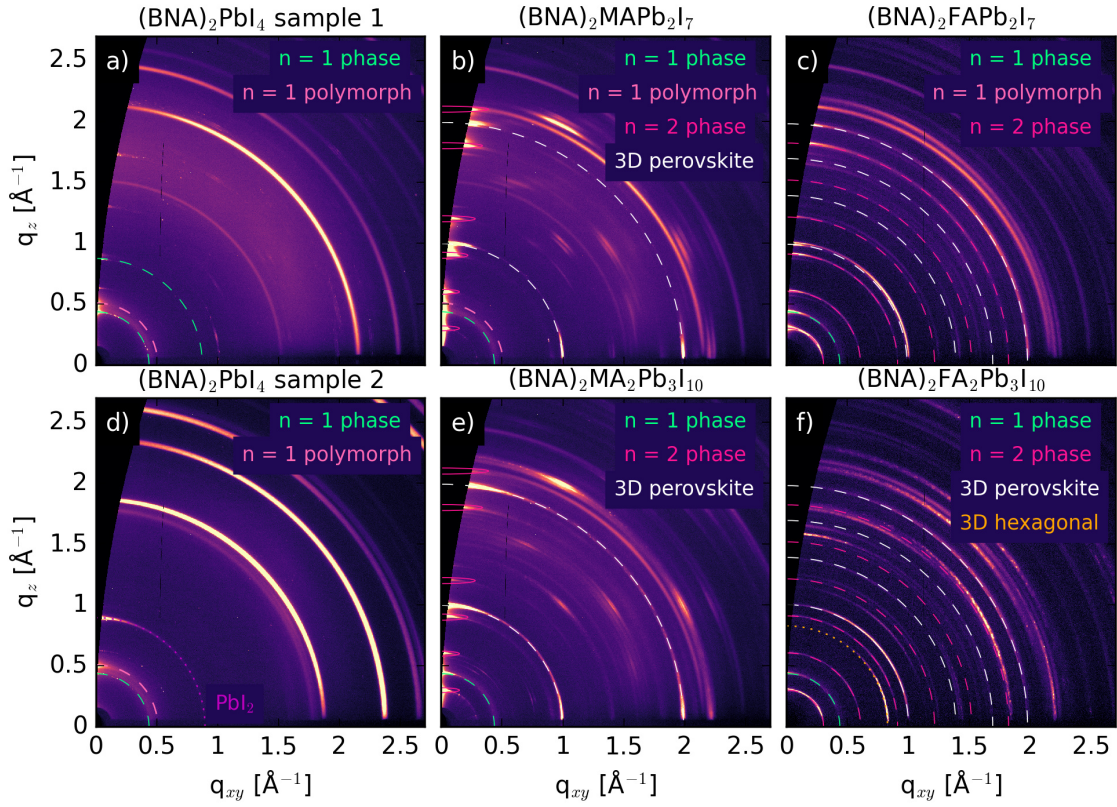


Figure 6.3.: GIWAXS reciprocal space maps of BNA iodide-based samples deposited onto ITO-coated glass at 0.3° angle of incidence showing structures within the sample bulk after annealing.

into the poly_3 phase and PbI_2 under intense annealing treatment.

6.2.3. BNAI-MA based $\tilde{n} = 2, 3$ compositions

The incorporation of MA^+ as a small cation into 2D perovskite was studied for compositions with $\tilde{n} = 2$ and $\tilde{n} = 3$ by *in situ* and *ex situ* GIWAXS, the results are summarized in Fig. 6.6, Fig. 6.5 and Fig. 6.3. The crystallization of the sample with $(\text{BNA})_2\text{MAPb}_2\text{I}_7$ composition $\tilde{n} = 2$, similarly to $\tilde{n} = 1$, involved multiple $n = 1$ polymorphs: poly_2 and $n = 1$ phases started their rapid formation immediately with the 3D perovskite phase once the annealing process started, followed by the slow formation of the $n = 2$ phase. When annealing was over, $n = 1$ phase showed its conversion into poly_3 phase, like in the $\tilde{n} = 1$ composition. As a result, the final sample showed a stable $n = 1$ phase with c like poly_1 in $n = 1$ sample (Tab. 6.1). The formation of the 3D perovskite phase and 2D $n = 2$ phase directly influenced the lattice parameter of the $n = 1$ phase: the heating energy possibly did not influence the size of the spacer cation in the $n = 1$ phase and was involved in the formation of other phases. The GIWAXS patterns acquired at different angles of incidence showed that 3D perovskite phase with the $n = 1$ phase and poly_3

$n = 1$ polymorph were formed closer to the surface, while $n = 2$ phase was found closer to the substrate. This explains the crystallization sequence, since the annealing was done by the halogen lamp. Similarly to the case of the $\tilde{n} = 1$ composition, the resulting $n = 1$ and $n = 2$ phases show in the preferred vertical orientation. Besides that, since the $n = 1$ phase was localized closer to the surface, and it is metastable, it converted into a more stable poly_3 polymorph with a shorter out-of-plane unit cell parameter c . This behavior of the $n = 1$ phase seems to be a common feature for the BNA spacer cation.

The $\tilde{n} = 3$ BNAI-MA composition in contrast displayed the appearance of the solvent-based intermediate phase, namely $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ solvent complex identified by its reflections at $|q| = 0.46 \text{ \AA}^{-1}$, $0.51 \text{ \AA}^{-1}$ and $0.65 \text{ \AA}^{-1}$ exactly at the start of the annealing treatment, as the scattering data suggests (Fig. 6.6 and Fig. 6.5(b)) [152]. The MA-based intermediate phase converted into the 3D perovskite phase closer to the surface, while MA-containing $n = 2$ phase formed closer to the substrate. As a result, the 2D $n = 1$ phase occupied the space between these two phases. The resulting $n = 1$ phase was vertically oriented, its scattering intensity increased once the annealing was over, together with 3D perovskite phase, unlike for $\tilde{n} = 2$ sample where $n = 1$ phase converted into the poly_3 polymorph after annealing. The out-of-plane XRR measurements (Fig. 6.4) supported the stabilization of $n = 1$ phase in $\tilde{n} = 3$ composition, whereas $n = 1$ phase in $\tilde{n} = 2$ sample due to its localization at the sample surface could easily convert into the poly_3 $n = 1$ polymorph. The presence of Kiessig oscillations suggests that the thickness of the prepared films can be estimated as $\sim 30 \text{ nm}$, with the lowest roughness within $\tilde{n} = 1$ sample, as the oscillations have the highest amplitude. The thickness is similar for different compositions due to the same precursor solution concentration and fabrication conditions. The XRR curve from the sample with $\tilde{n} = 3$ in the q -range of $0.05\text{--}0.15 \text{ \AA}^{-1}$ lacks some measurement points due to suboptimal absorber utilization. The sample with $\tilde{n} = 2$ has higher roughness than the composition with $\tilde{n} = 3$ as suggested by the comparison of the oscillations amplitude, which might be due to the presence of $n = 1$ polymorph, while the latter composition exhibited a well-oriented $n = 1$ phase.

Samples with MA as central cation and $\tilde{n} = 2, 3$ compositions showed similar trends of the scattering intensity evolution, including its saturation, with the exception of $n = 1$ phase and $n = 1$ polymorph. 2D RP $n = 1$ and $n = 2$ phases in both MA-based compositions are vertically oriented (Fig. C.4(a) and Fig. C.5(a)), which is in turn beneficial for using them as top layers on 3D perovskite compositions to prevent potential degradation.

6.2.4. BNAI-FA-based $\tilde{n} = 2, 3$ compositions

The incorporation of FA^+ as a small cation into 2D perovskites was studied for $\tilde{n} = 2$ and $\tilde{n} = 3$ compositions with *in situ* and *ex situ* GIWAXS, the results are summarized in Fig. 6.8, Fig. 6.5 and Fig. 6.3. Sample with $\tilde{n} = 2$ showed the crystallization starting from liquid-air interface, resulting in fast formation of 3D cubic perovskite phase closer to

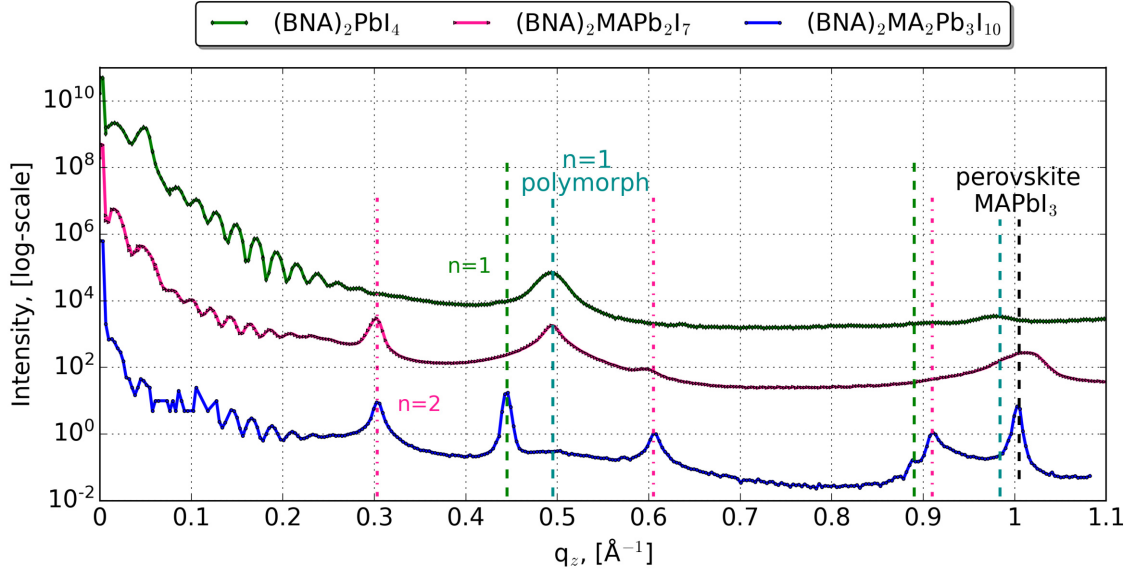


Figure 6.4.: XRR curves from BNA-, MA- and iodide-based 2D perovskite compositions with target dimensionalities $\tilde{n} = 1-3$. All thin films deposited onto glass/ITO substrates. The Bragg peaks are well developed, but note that the shape in the low- q region is slightly unusual, probably due to significant roughness of the interfaces and maybe also waviness of the top surface. For details, see text.

the surface. This was followed by $n = 2$ phase formation below and $n = 1$ phase closer to the substrate. An $n = 1$ polymorph started its formation once $n = 1$ phase scattering intensity saturated. The XRR measurements, displayed in Fig. 6.4 show that $n = 1$ polymorph in FA-based samples has a shorter unit cell parameter c in comparison to the $n = 1$ polymorph in $\tilde{n} = 1$ and MA-based compositions, which might be associated with the influence of the small cation. The orientation profiles of different phases within the sample and *ex situ* GIWAXS maps showed a more random orientation unlike 2D phases in MA-based compositions, as it can be seen in Fig. C.4 and Fig. C.5. The comparison of iodide-based samples with $\tilde{n} = 2$ (Fig. 6.3) showed that in FA-based sample $n = 2$ phase fraction is ~ 3 times more than that of an $n = 1$ phase, whereas the MA-based sample had ~ 3 times more of $n = 1$ phase than $n = 2$ phase, which might originate from the effects of small cations on thin film structure. The XRR data of thin films based on FA deposited on glass/ITO/TiO₂, displayed in Fig. 6.7, do not show Kiessig oscillations, which can be attributed to either differences in small cations or substrate effects that cause an increase in roughness.

The BNAl-FA-based composition with $\tilde{n} = 3$ target dimensionality started its crystallization with formation of hexagonal phase on the sample surface, followed by cubic perovskite and $n = 2$ phase growth. Like in $\tilde{n} = 2$ sample, the $n = 1$ phase crystallized last closer to the substrate. After 60 s of the annealing treatment, hexagonal phase scattering intensity started to decrease until the end of the heating treatment, indicating

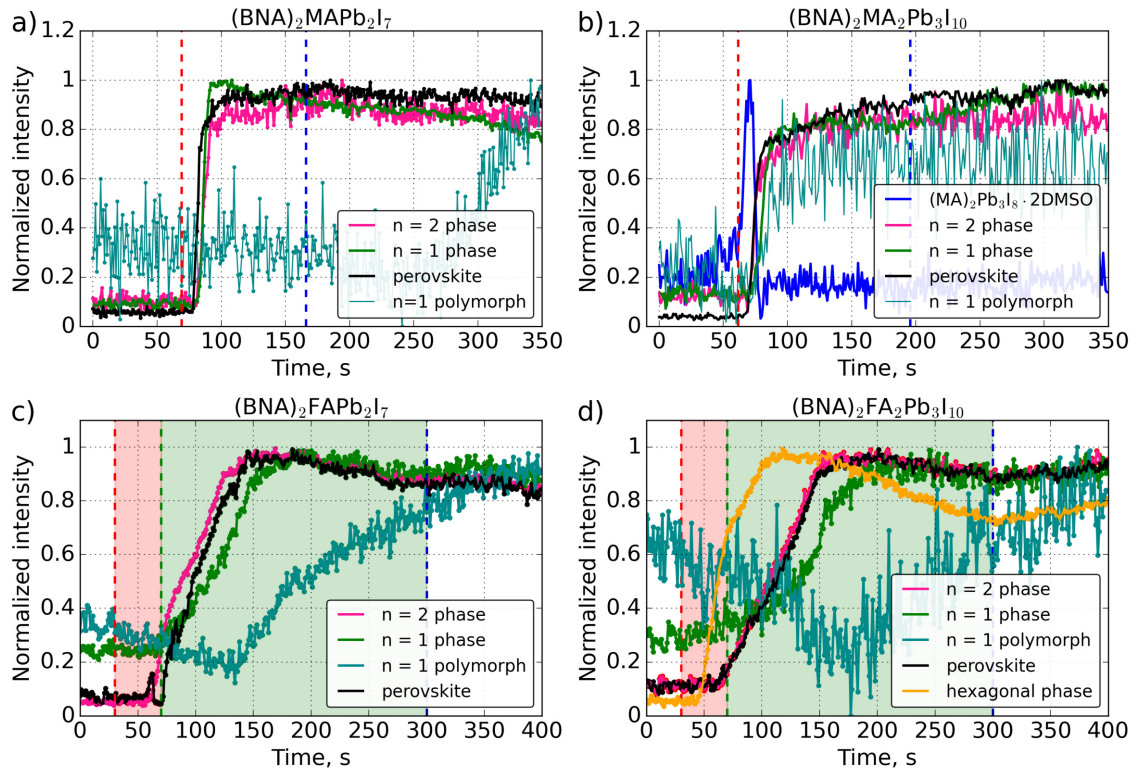


Figure 6.5.: Integrated scattering intensities of the structures during crystallization of BNA iodide-based samples: (a) $(\text{BNA})_2\text{MAPb}_2\text{I}_7$; (b) $(\text{BNA})_2\text{MA}_2\text{Pb}_3\text{I}_{10}$; (c) $(\text{BNA})_2\text{FAPb}_2\text{I}_7$ and (d) $(\text{BNA})_2\text{FA}_2\text{Pb}_3\text{I}_{10}$.

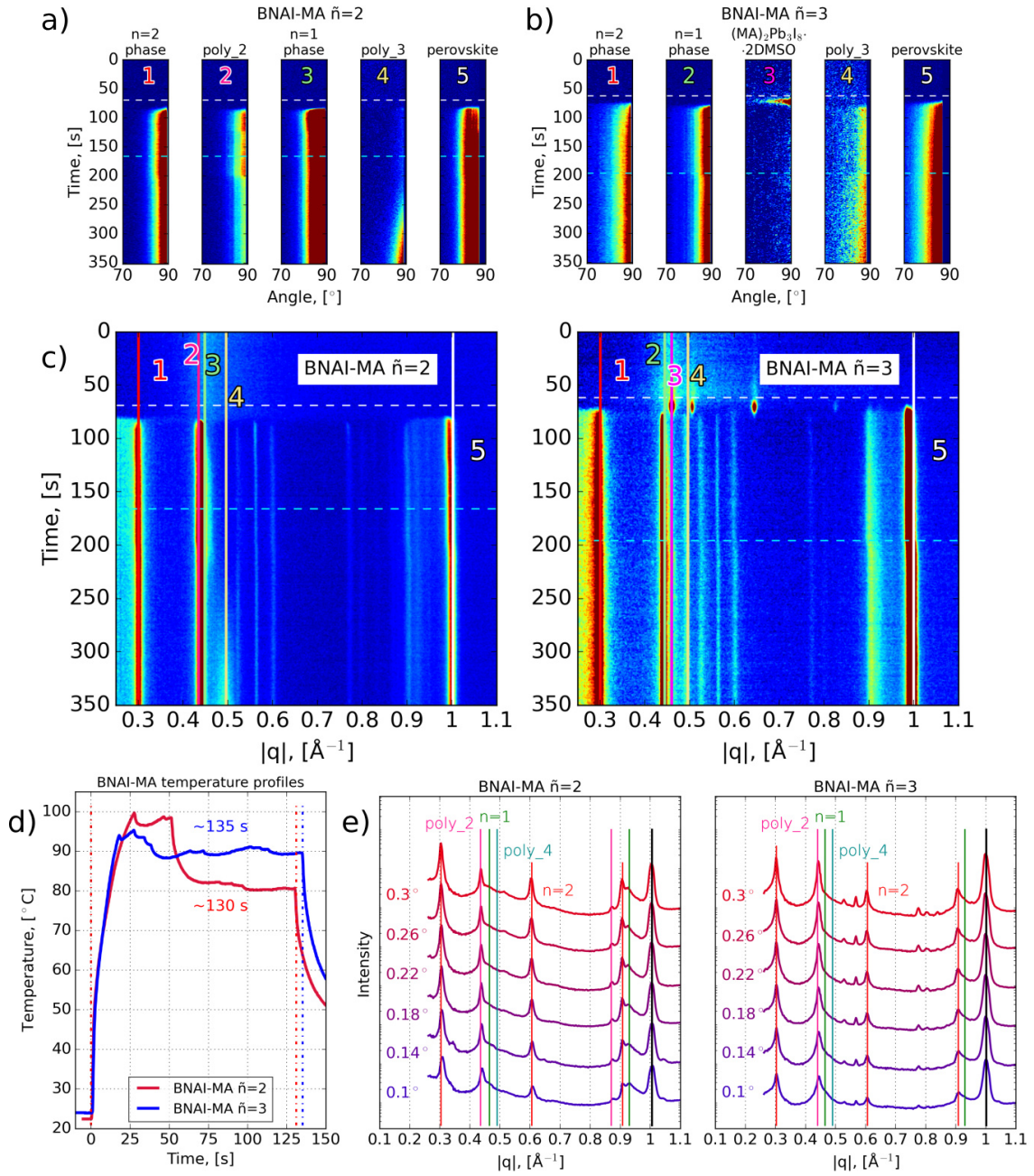


Figure 6.6.: Orientation profiles of different phases in (a) (BNA)₂MAPb₂I₇ and (b) (BNA)₂MA₂Pb₃I₁₀ samples during annealing procedures. Azimuthally integrated synchrotron-based GIWAXS patterns in waterfall plots, displaying the crystallization of (c) (BNA)₂MAPb₂I₇ and (d) (BNA)₂MA₂Pb₃I₁₀ compositions; e) Annealing profiles for both compositions; f) Integrated intensities of angular-dependent GIWAXS scans after annealing with marked phases.

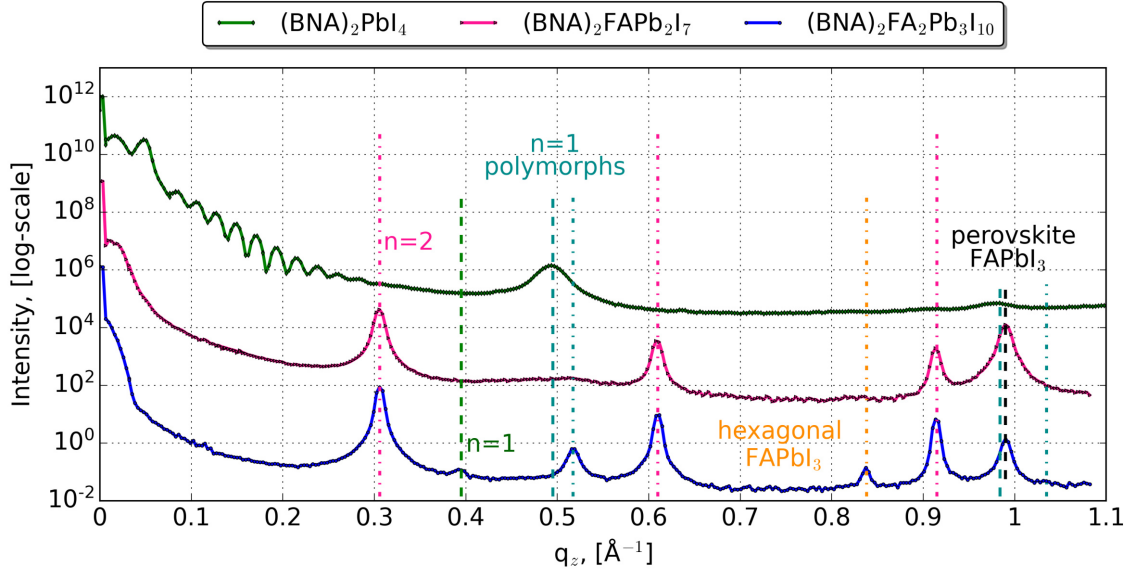


Figure 6.7.: XRR curves from BNA-, FA- and iodide-based 2D perovskite compositions with target dimensionalities $\tilde{n} = 1-3$. The $\tilde{n} = 1$ thin film was deposited onto glass/ITO substrate, while FA-based thin films were deposited onto glass/ITO/TiO₂ substrates. The Bragg peaks are well developed, but note that the shape in the low- q region is slightly unusual, probably due to significant roughness of the interfaces and maybe also waviness of the top surface. For details, see text.

its conversion into other phases, including the desired perovskite phase. Besides that, more of cubic perovskite was formed in comparison to the $\tilde{n} = 2$ FA-based composition. The cubic perovskite phase started its saturation simultaneously with the $n = 2$ phase. Similarly to the $\tilde{n} = 2$ BNAI-FA composition, crystallites are more randomly oriented, than in MA-based compositions, as it can be seen in Fig. C.4 and Fig. C.5. This possibly comes from the nature of FA-based 2D perovskite compositions which are often not able to form $n > 2$ phases due to its tendency to form 2H hexagonal phase, which is energetically more favorable [76]. Other remarkable difference between FA and MA small cation incorporation comes from multiple orientations of the $n = 2$ phase in the FA-based compositions, as it is displayed in Fig. C.5. For MA-based compositions, vertical orientation was preferable, while for FA-based compositions two orientations were observed: mainly vertical and under 51° for the $\tilde{n} = 2$ composition and mainly under 57° and some vertical orientation for the $\tilde{n} = 3$ composition. Finally, thin films with $\tilde{n} = 1-3$ and MA as a small cation have a low roughness, which leads to Kiessig oscillations in XRR data, and the estimated thickness of 30 nm, while FA-based samples do not show these features due to the roughness.

The 2D perovskite compositions, based on BNA and iodide, showed structural diversity of the $n = 1$ 2D phases, which are being formed upon thermal annealing. In essence, $\tilde{n} = 1$ composition involved various phases during thin film growth, including the target

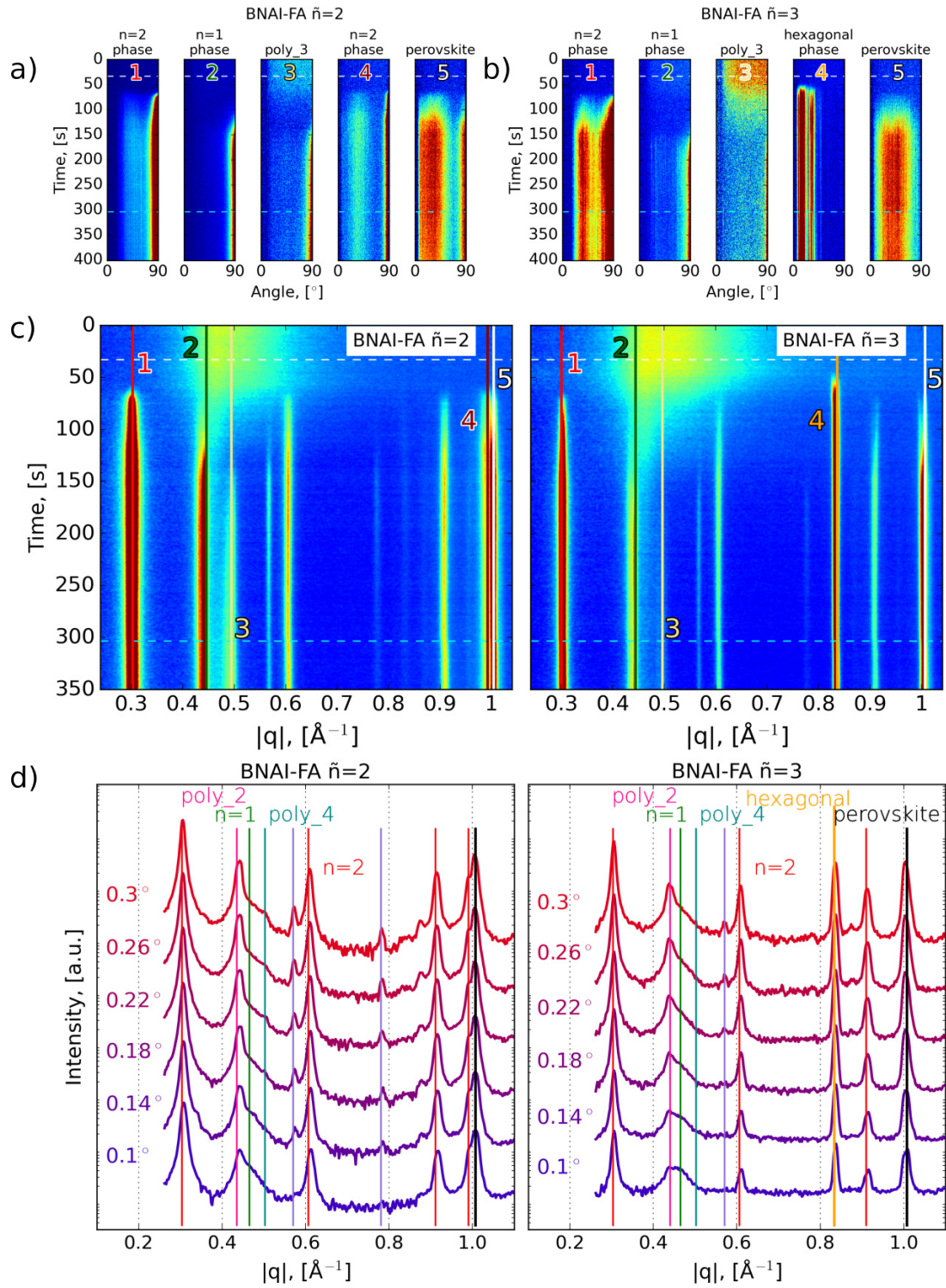


Figure 6.8.: Orientation profiles of different phases in (a) $(\text{BNA})_2\text{FAPb}_2\text{I}_7$ and (b) $(\text{BNA})_2\text{FA}_2\text{Pb}_3\text{I}_{10}$ samples during annealing procedures. Azimuthally integrated synchrotron-based GIWAXS patterns in waterfall plots, displaying the crystallization of (c) $(\text{BNA})_2\text{FAPb}_2\text{I}_7$ and (d) $(\text{BNA})_2\text{FA}_2\text{Pb}_3\text{I}_{10}$ samples; e) Annealing profiles for both samples; f) Integrated intensities of angular-dependent GIWAXS scans after annealing with marked phases.

$n = 1$ phase, marked in current work as poly_2 [150]. This phase was formed upon annealing, while once the halogen lamp was switched off, presumably a thermal relaxation of the BNA spacer cation took place, which resulted in conversion into a polymorph with a shorter c parameter. It turned out to be a common feature for compositions with $\tilde{n} = 1-3$ as well as for the MA and FA small cations, which suggests that it is based on the nature of BNA and iodide interactions.

6.3. BNA- and bromide-based perovskites

In current section the influence of a different halide, namely bromide instead of iodide, on crystallization pathways and final films, based on the BNA spacer cation, was investigated.

6.3.1. $(\text{BNA})_2\text{PbBr}_4$ $\tilde{n} = 1$ composition

The effect of changing halide within the $\tilde{n} = 1$ composition of RP BNA-based composition is investigated. The vertical orientation of the $n = 1$ phase with its reflection at $|q| = 0.38 \text{ \AA}^{-1}$ was observed in the film, the degree of which was predefined during spin-coating procedure and did not change significantly during the annealing procedure, as it can be seen in Fig. C.6. For the sample 1 the orientation was more random in the beginning, rapidly changing to vertical, whereas for the sample 2 the orientation was strongly vertical with slight changes towards random before the annealing treatment. The main feature of the BNA-Br $\tilde{n} = 1$ composition is the ability to stabilize $n = 1$ phase and prevent the formation of $n = 1$ polymorphs, which was observed for the BNA-I $\tilde{n} = 1$ composition (Fig. 6.2).

Another interesting feature was observed on GIWAXS patterns with different angles of incidence, like in BNAI $\tilde{n} = 1$ composition: a refraction effect [271], resulting in doubling of the $n = 1$ phase reflections at angles of incidence between 0.12° and 0.2° , as displayed in Fig. C.2(b). This supports the conclusion that the BNA spacer cation forms thin films with good surface condition, which is beneficial for using them as capping layers on top of 3D perovskites to prevent its degradation under ambient conditions.

The $\tilde{n} = 1$ composition showed the formation of one $n = 1$ phase with preferred vertical orientation after spin-coating procedure and before the annealing treatment. This is a positive influence of Br halide, which initiates the formation of the desired phase within the coated film. This seems to be a common outcome of deposition of the 3D and 2D perovskite compositions, based on bromide, as it was observed for MAPbBr_3 in Subsec. 5.2.5 and for bromide-rich phase in the mixed halide compositions [39].

6.3.2. BNABr-MA based $\tilde{n} = 2, 3$ compositions

The incorporation of the MA as small cation into BNA bromide-based compositions was studied next. The crystallization of the sample with $(\text{BNA})_2\text{MAPb}_2\text{Br}_7$ composition

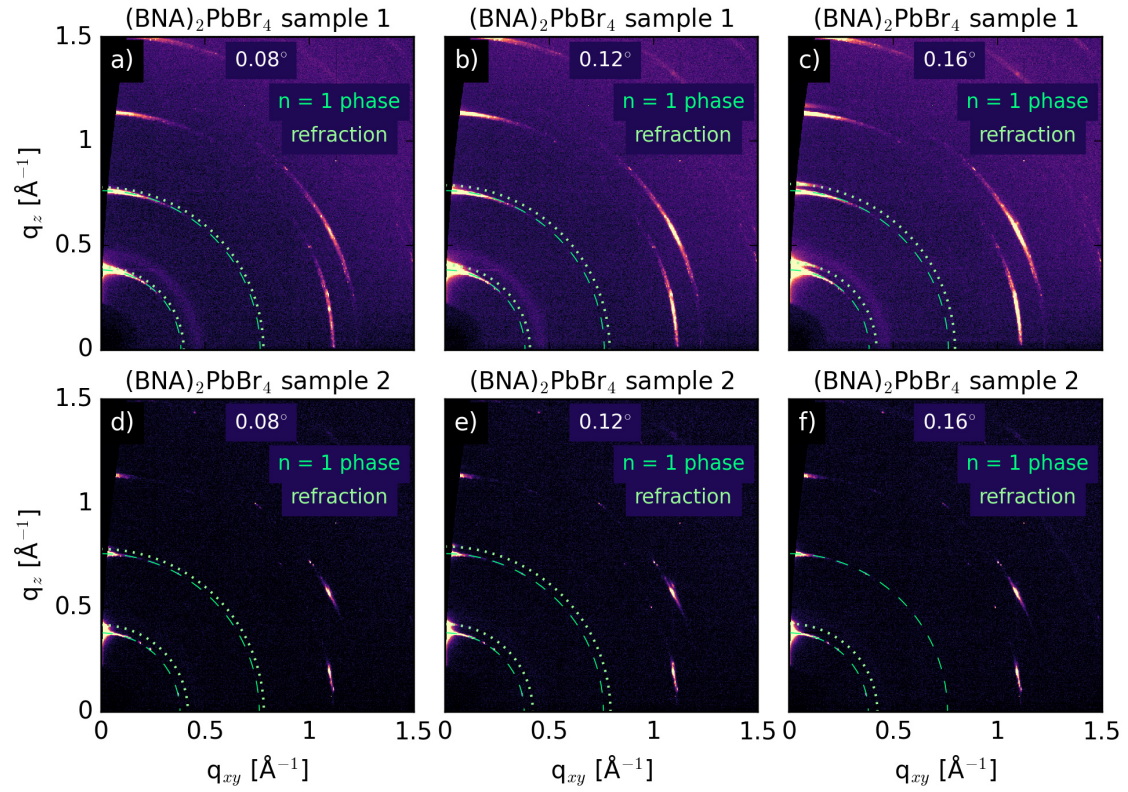


Figure 6.9.: GIWAXS data with marked refraction effect [271] from $n = 1$ phase and $n = 1$ polymorph in $(\text{BNA})_2\text{PbBr}_4$ 2D RP composition and other phases. Sample 1 measured at the angle of incidence (a) $\alpha_i = 0.08^\circ$, (b) $\alpha_i = 0.12^\circ$, (c) $\alpha_i = 0.16^\circ$ and sample 2 measured at the angle of incidence (d) $\alpha_i = 0.08^\circ$, (e) $\alpha_i = 0.12^\circ$, (f) $\alpha_i = 0.16^\circ$.

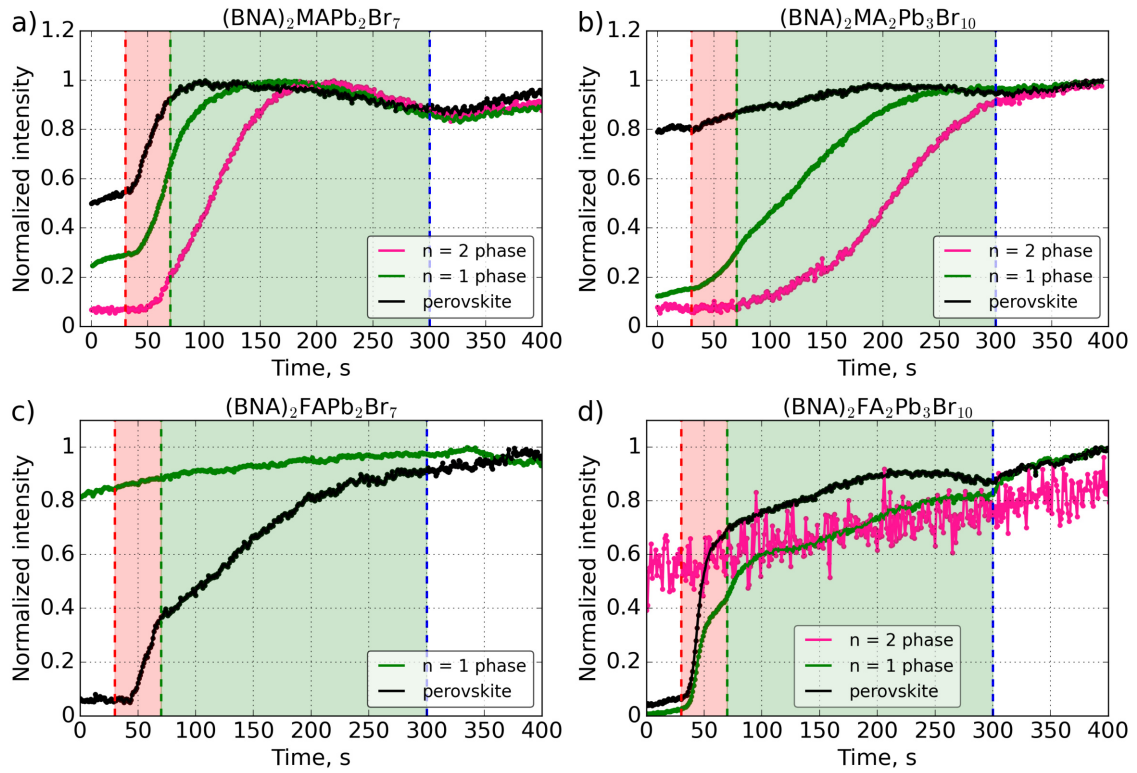


Figure 6.10.: Integrated scattering intensities of the structures during the annealing step of BNA bromide-based samples: (a) $(\text{BNA})_2\text{MAPb}_2\text{Br}_7$; (b) $(\text{BNA})_2\text{MA}_2\text{Pb}_3\text{Br}_{10}$; (c) $(\text{BNA})_2\text{FAPb}_2\text{Br}_7$ and (d) $(\text{BNA})_2\text{FA}_2\text{Pb}_3\text{Br}_{10}$.

($\tilde{n} = 2$) is shown in Fig. 6.10(a). Already during spin-coating procedure, three phases were formed, namely $n = 1$ phase with its reflection at $|q| = 0.38 \text{ \AA}^{-1}$, $n = 2$ phase with reflection at $|q| = 0.28 \text{ \AA}^{-1}$ and MAPbBr₃ cubic perovskite [238], indicated by the reflection at $|q| = 1.06 \text{ \AA}^{-1}$. All observed phases showed preferred vertical orientation. The annealing procedure activated the growth of the formed structures, their scattering intensities increased (Fig. 6.10(a)). After ~ 70 s of annealing, perovskite cubic phase showed its scattering intensity saturation, followed by $n = 1$ and $n = 2$ phases approaching their scattering intensities maxima after 150 s and 200 s, respectively. This formation sequence is similar to the iodide-based $\tilde{n} = 2$ composition, however for bromide-based sample the postponed formation dynamics of $n = 1$ and $n = 2$ phases was more pronounced. The crystallization sequence defined the layout of the sample after annealing (Fig. C.11), it suggests that the formation of thin film started from top of the sample due to the annealing geometry (Fig. 6.1).

The $\tilde{n} = 3$ BNABr-MA composition showed a similar to $\tilde{n} = 2$ crystallization pathway, as shown in Fig. 6.10(a),(b). The remarkable difference is following: the 3D perovskite phase was mainly formed before annealing process, which can be estimated from the initial scattering intensity as $0.8 \cdot I_{max}$. The presence of higher fraction of the perovskite phase within the initial sample in $\tilde{n} = 3$ composition slowed down the crystallization rate of all identified structures and further postponed the growth of 2D RP phases, the formation of $n = 1$ and $n = 2$ 2D phases was finished at ~ 250 s and ~ 350 s of the experiment, respectively. The layout of the sample after annealing identical to that of an $\tilde{n}=2$ composition: $n = 1$ phase is localized between cubic perovskite, which is closer to the surface, and $n = 2$ phase, localized closer to the substrate.

Samples with MA as central cation and $\tilde{n} = 2$ or $\tilde{n} = 3$ compositions show similar trends in terms of scattering intensity evolution, including their saturation, with the exception of the rates, since the presence of the major fraction of the 3D perovskite phase closer to the sample surface slowed down the crystallisation speed and postponed the formation of 2D phases. This similar trend also resulted in the similar ratios of the phases formed within the deposited films, as it is displayed in Fig. C.7.

6.3.3. BNABr-FA based $\tilde{n} = 2, 3$ compositions

The effect of FA small cation incorporation into BNA bromide-based perovskites was studied next. Sample with $\tilde{n} = 2$ composition showed the formation of major fraction of $n = 1$ phase, $0.8 \cdot I_{max}$ before annealing treatment (Fig. 6.10(c)). This phase saturated until the end of the annealing procedure. FAPbBr₃ perovskite phase [272], characterized by its (100) reflection at $1.05 \text{ \AA}^{-1}$, started to form closer to the substrate at 15 s of annealing, its crystallization rate depended on annealing power: at 150 W it was rapid, followed by slower growth at 85 W until the end of the experiment. The formation sequence reflects the sample layout based on GIWAXS measured after annealing (Fig. C.11). Besides discussed structures, an additional phase was observed with its reflections laying on $q_{xy} = 1.72 \text{ \AA}^{-1}$

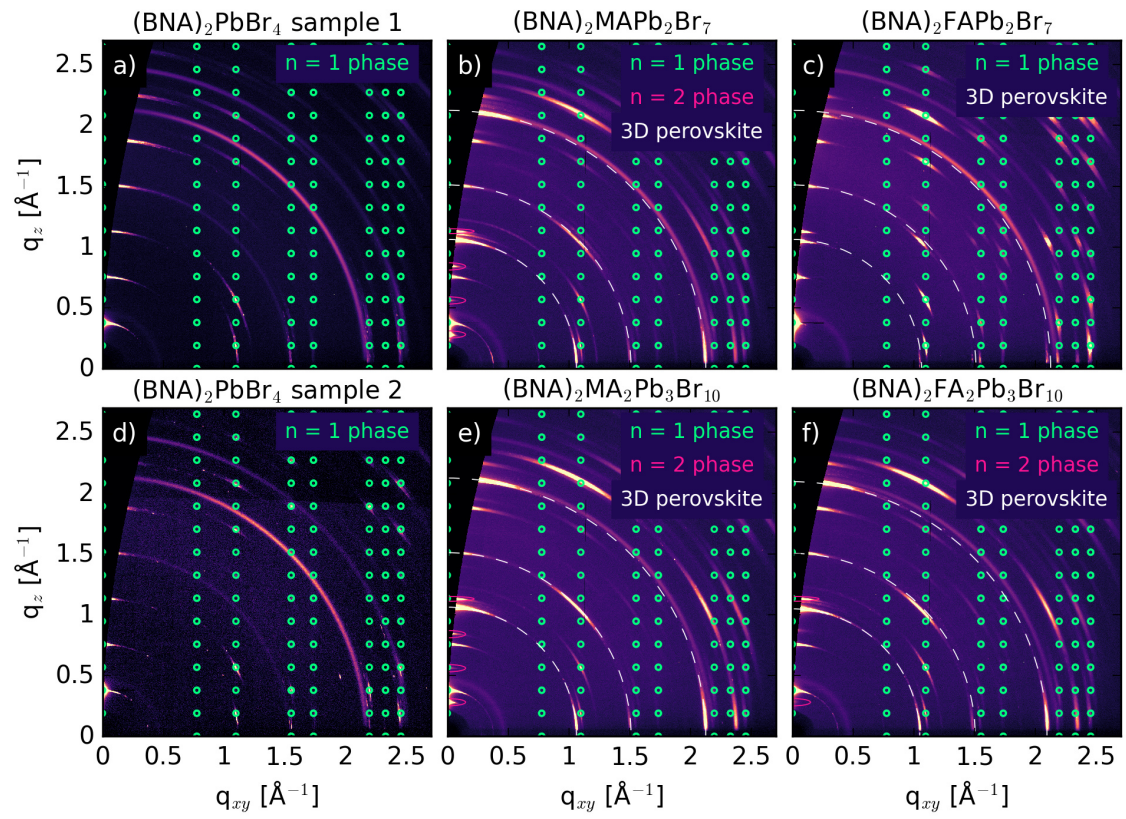


Figure 6.11.: GIWAXS reciprocal space maps of BNA bromide-based samples with 0.3° angle of incidence and marked structures within the whole film after annealing.

axis. The remarkable difference between $\tilde{n} = 2$ iodide and bromide based compositions is following: in compositions with Br as a halide, FA cation leads to higher degree of $n = 1$ phase orientation than MA cation, while for iodide composition the opposite trend was observed (compare Fig. C.9 and Fig. C.4).

The FA-based BNA-Br $\tilde{n} = 3$ composition showed a different crystallization pathway, just before annealing treatment the scattering intensities from the 2D $n = 1$ phase and 3D perovskite phases were slowly increasing. The start of the annealing process resulted in rapid scattering intensity increase of 3D cubic perovskite indicating solvent evaporation followed by $n = 1$ phase formation. Unlike in $\tilde{n} = 2$ composition, $n = 1$ phase was localized closer to the substrate, while 3D perovskite phase was found closer to the surface (Fig. C.11). The scattering intensity of 2D $n = 2$ phase was increasing, which supports the hypothesis of its role as an intermediate link between $n = 1$ phase and 3D perovskite in BNABr-FA compositions.

Samples with FA as a central cation showed different trends of scattering intensity evolution. In $\tilde{n} = 2$ composition $n = 1$ phase was closer to the surface, while cubic perovskite was formed closer to the substrate, in $\tilde{n} = 2$ composition it was the other way around. In $\tilde{n} = 3$ FA-based composition $n = 2$ phase behaved as an intermediate link between the 2D $n = 1$ phase and 3D perovskite phase. All 2D phases in BNABr-FA compositions showed a preferred vertical orientation, for $\tilde{n} = 2$ composition it was more pronounced, while for $\tilde{n} = 3$ composition 2D phases were slightly less oriented. This might be a consequence of FAPbBr₃ perovskite phase formation on the top of the sample, which slightly suppressed the formation of more oriented 2D phases, as there was more of 3D perovskite in $\tilde{n} = 3$ composition (Fig. C.8).

6.4. DJ $\tilde{n} = 1$ 2D perovskite compositions

This section is focused on *in situ* growth characterization of 2D perovskites based on PDMA and PDEA, displayed in Fig. 3.10(a), studied by GIWAXS and XRR. For PDMA, $\tilde{n} = 1$ layered perovskite compositions based on iodide and bromide halides, whereas for PDEA only the composition based on iodide was studied (Tab. 6.2). The resulting structures formed DJ 2D phases, displayed in Fig. 3.10(b) [164]. All studied compositions were deposited onto 5 mm thick TiO₂/FTO-coated glass substrates. The substrates were fixed to a sample table in the spin-coating chamber [36] with heat-resistant adhesive tape. After alignment, 60 μ L of the corresponding precursor solution was applied on the substrate and spin-coated for 10 s at 1000 rpm and 30 s at 4000 rpm, as displayed in Fig. 6.1(a). The annealing process was conducted using a halogen lamp positioned 40 mm from the sample and the surface temperature of the sample was estimated using a pyrometer directed at the sample surface. The annealing process was monitored by visual inspection of the scattered reflections from different phases. The sketch of the spin-coating chamber is presented in Fig. 6.1(b).

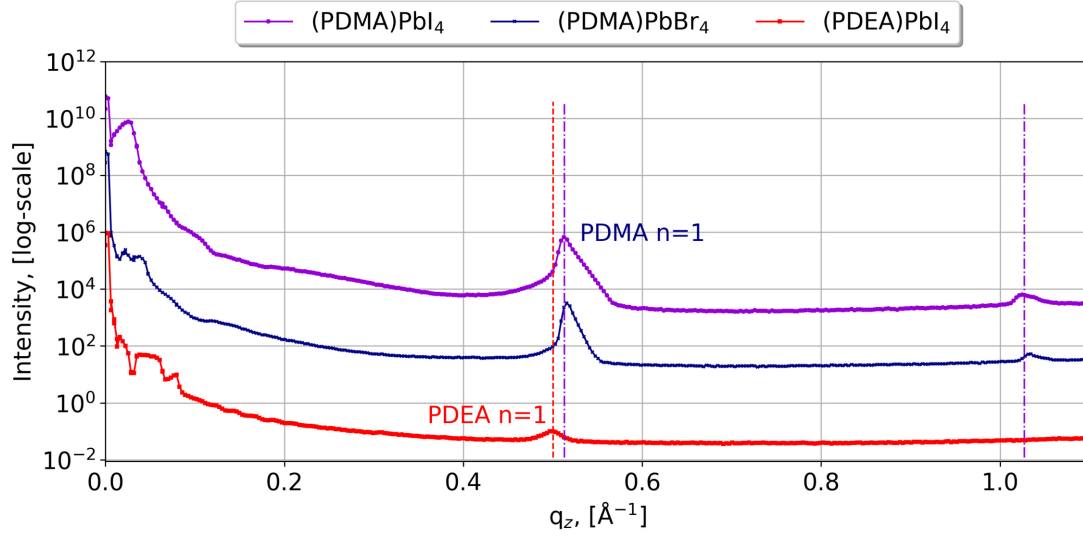


Figure 6.12.: XRR curves from (PDEA)PbI₄, (PDMA)PbI₄ and (PDMA)PbBr₄ compositions. All thin films were deposited onto glass/ITO/TiO₂ substrates. The Bragg peaks are well developed, but note that the shape in the low- q region is slightly unusual, probably due to significant roughness of the interfaces and maybe also waviness of the top surface. For details, see text.

Table 6.2.: Structural composition of the studied samples and solvents.

Sample	Solvent mixture	Substrate
(PDMA)PbI ₄	DMF:DMSO (4:1)	Glass/ITO/TiO ₂
(PDMA)PbBr ₄	DMF:DMSO (4:1)	Glass/ITO/TiO ₂
(PDEA)PbI ₄	DMF:DMSO (4:1)	Glass/ITO/TiO ₂

6.4.1. Results extracted from XRR

XRR measurements of the samples showed the presence of $n = 1$ 2D DJ phases in all studied compositions (Fig. 6.12), for PDMA-based composition the Bragg peaks are located at 7.23° for (PDMA)PbI₄ (Tab. 6.3) and 7.27° for (PDMA)PbBr₄ (Tab. 6.4), whereas for the PDEA-based composition the spacing is larger, the Bragg peak is located at 7.03° (Tab. 6.5). This result is in a good agreement with the difference between spacer cations in the composition (PDMA or PDEA) as well as halides (I or Br). For PDMA-based compositions in the XRR data two, an intense first ($0.513 \text{ \AA}^{-1}$) and a less intense second ($1.026 \text{ \AA}^{-1}$) order reflections were observed, while for the PDEA-based composition only the first order reflection with a low intensity was identified. This indicates the presence of a preferred orientation for PDMA-based samples, while for the PDEA-based sample $n = 1$ phase has a more random orientation, as it can be seen from the GIWAXS data (Fig. 6.17(b,c)) Nevertheless, the (PDEA)PbI₄ compositions showed the presence of Kiessig oscillations in the q_z range of $0.12\text{--}0.2 \text{ \AA}^{-1}$, which suggest thin film thickness of 30 nm,

Table 6.3.: Out-of-plane lattice parameter (c) for (PDMA)PbI₄ $n = 1$ structure, extracted from the experiment, comparison to the literature value [178].

Literature [178]	GIWAXS sample 1 ("thick")	GIWAXS sample 2 ("thin")	XRR sample 2 ("thin")
12.28 Å (7.19°)	12.39 Å	12.46 Å	7.23°

Table 6.4.: Out of plane lattice parameter (c) for (PDMA)PbBr₄ $n = 1$ structure, extracted from the experiment, comparison to the literature value [178].

Literature [178]	GIWAXS	XRR
12.22 Å (7.26°)	12.37 Å	7.27°

similarly to the BNA-based compositions, displayed in Fig. 6.4. This analogy is caused by the same fabrication parameters and concentration of the precursor solution. The difference in the amplitude of oscillations might originate from higher roughness of the DJ-based phases. The samples with PDEA as spacer cation were smoother than that with PDMA, which might be due to the differences in spacer orientation, as the latter one is oriented out-of-plane.

6.4.2. Results extracted from GIWAXS

(PDMA)PbI₄ $n = 1$ composition

The (PDMA)PbI₄ composition was studied with two annealing profiles: a slow and a rapid one, pyrometer measurements are displayed in Fig. 6.13. Both times, the scattering intensity from the $n = 1$ phase approached its maximum at $\sim 93^\circ\text{C}$, after 132 s and 25 s, respectively, as marked in Fig. 6.14. After approaching the "critical" temperature, the scattering intensity from the 2D perovskite started to decrease, possibly indicating material decomposition. In the case of slow annealing, $n = 1$ phase for sample 1 adapted preferred vertical orientation, as it was defined from the GIWAXS data, displayed in Fig. 6.16(a), which proves the sensitivity of 2D materials to annealing ramps and highlights the necessity of the careful experimental design.

The GIWAXS data of the resulting samples with marked structures is displayed in Fig. 6.15(a,b). The $n = 1$ phase has a strong vertical orientation, the scattering intensity from it is rather high (Fig. 6.16(a)), no substrate reflection was observed. This leads to the conclusion that slow annealing treatment results in the formation of a "thick" film. In the case of a rapid annealing (sample 2, Fig. 6.16(b)), $n = 1$ phase reflection displayed random orientation, only the first reflection at $0.5 \text{ \AA}^{-1}$ being intense, while higher order reflections were rather weak. The substrate reflection was strong, suggesting that the resulting film is "thin" due to material evaporation and decomposition as a consequence of the excessive annealing. Fast annealing did not let all the composition to grow with strongly preferred

Table 6.5.: Out of plane lattice parameter (c) for (PDEA)PbI₄ $n = 1$ structure, extracted from the XRR experiment, comparison to the literature value [178].

Literature [178]	GIWAXS	XRR
12.73 Å (6.98°)	12.76 Å	7.03°

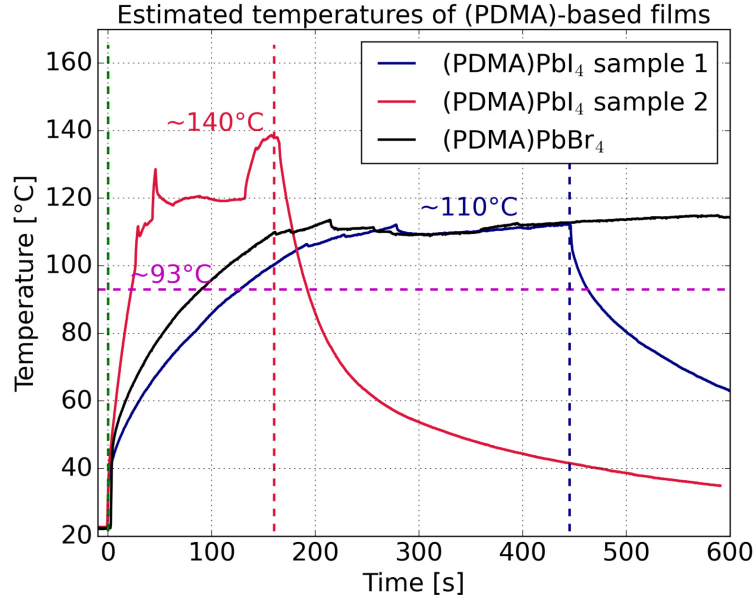


Figure 6.13.: Estimated temperature of (PDMA)PbI₄ samples measured by pyrometer.

orientation which resulted in random orientation. A comparison of the long unit cell parameters, summarized in Tab. 6.3, indicates that the "thick" film with a preferred vertical orientation tends to have a shorter c unit cell parameter than the "thin" film without preferred orientation, since a more random orientation allows for greater space for molecules in-plane, the resulting c parameter is larger. On the other hand, the literature value [178] of c is shorter, which might originate from differences in the fabrication method. For instance, based on the comparison of *ex situ* GIWAXS in current work and in published work [178], the latter one displayed more than one preferred orientation of $n = 1$ phase and was partially decomposed during fabrication, since PbI₂ was identified within the film.

(PDMA)PbBr₄ $n = 1$ composition

The scattering intensity evolution from the $n = 1$ phase within the $n = 1$ (PDMA)PbBr₄ composition during annealing procedure is presented in Fig. 6.15(c). The reflection from $n = 1$ phase at $0.5 \text{ \AA}^{-1}$ increased during annealing treatment due to the solvent evaporation and liquid-to-solid transition, and then started to decrease until the end of the annealing procedure, reflecting a potential misalignment, since the reflection position did not change, unlike for (PDMA)PbI₄. The GIWAXS data of the final film indicated the presence of

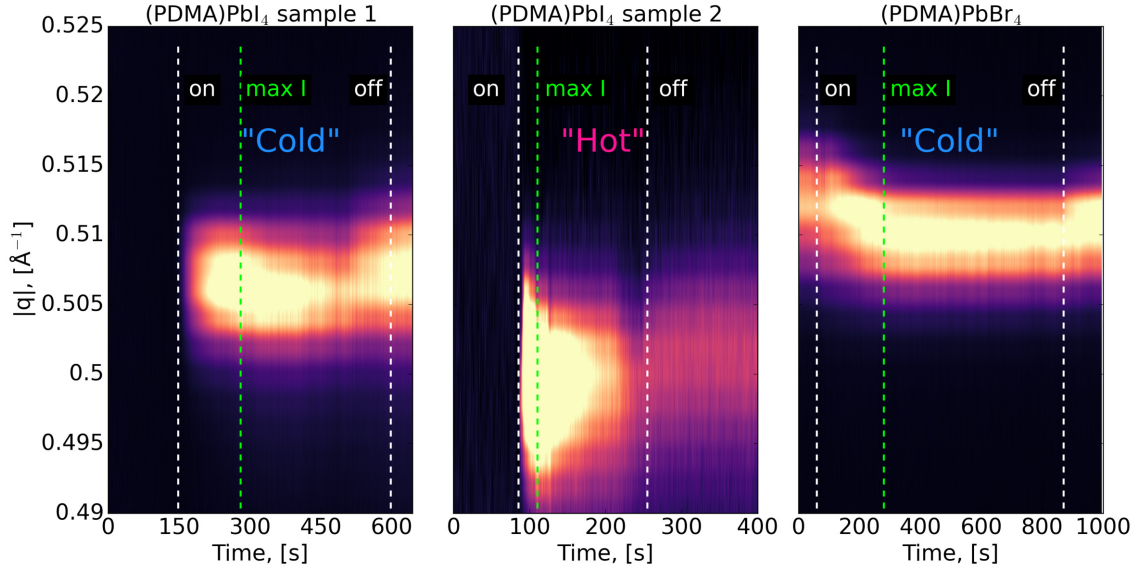


Figure 6.14.: GIWAXS data in waterfall plots during annealing of (PDMA)PbI₄ and (PDMA)PbBr₄ compositions, focused on the (100) reflection from $n = 1$ phase. White lines indicate the beginning and the end of annealing, while bright green (lime) line marks the moment when the maximum of the scattering intensity from the 2D DJ phase was detected.

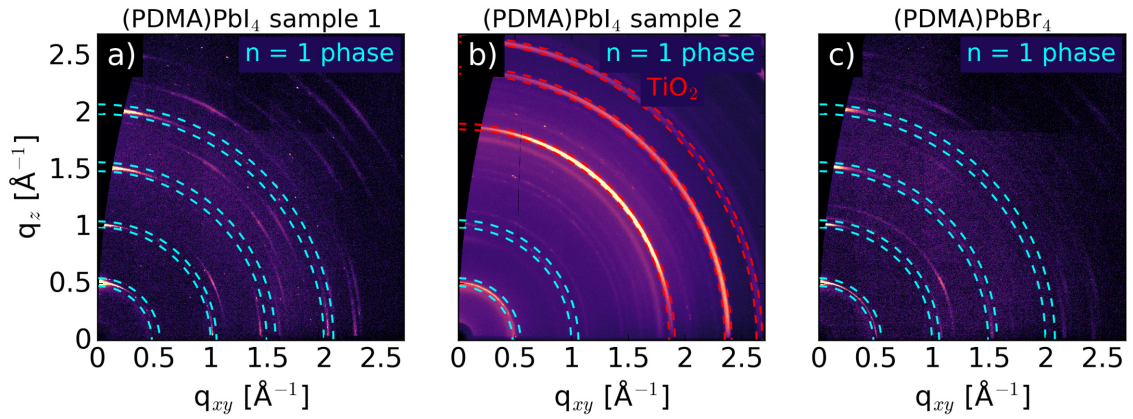


Figure 6.15.: GIWAXS reciprocal space maps of the PDMA-based DJ $n = 1$ 2D compositions deposited onto TiO₂-coated glass at 0.2° angle of incidence with marked reflections from $n = 1$ phase within the sample after annealing: (a)(PDMA)PbI₄ sample 1, (b)(PDMA)PbI₄ sample 2 and (c)(PDMA)PbBr₄.

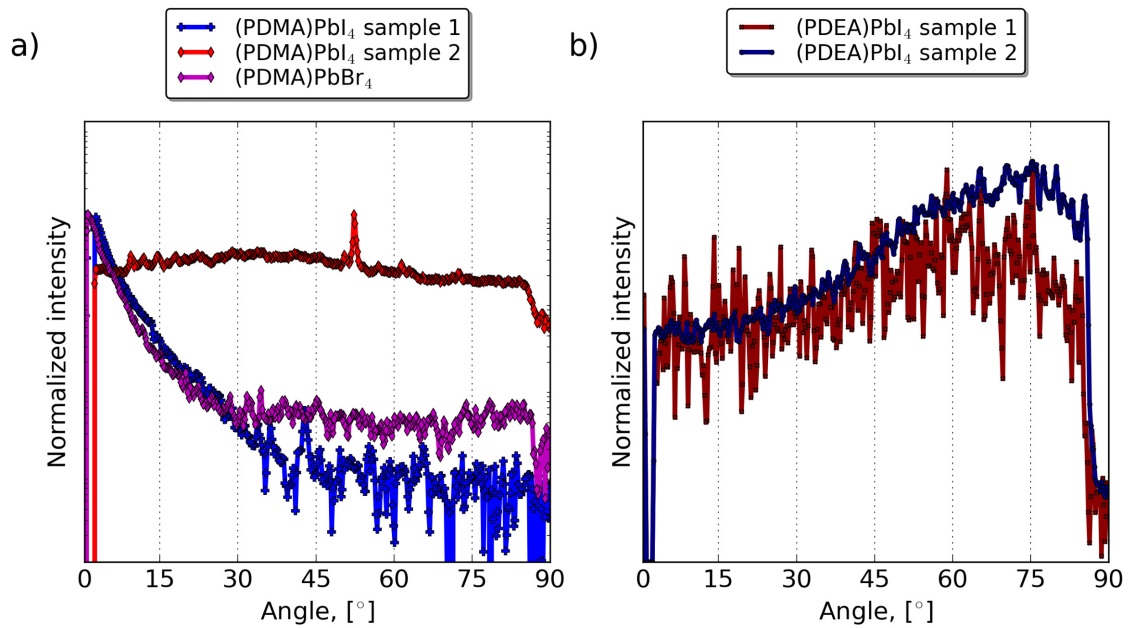


Figure 6.16.: Degree of orientation of $n = 1$ phase in (a) PDMA- and (b) PDEA-based $n = 1$ DJ 2D perovskite compositions.

preferable vertical orientation of the spacer cation (Fig. 6.16(a)) with a minor amount of randomly oriented crystallites. A direct comparison of the current work with the published results [178] suggests that the PDMA spacer cation is quite sensitive to overheating, thus even a slightly increased annealing temperature results in a more randomly oriented 2D DJ $n = 1$ phase. As a result, a slight smearing of the Bragg peaks was observed in the published data, while annealing at lower temperature for shorted period of time resulted in a vertical orientation of the spacer cation.

(PDEA)PbI₄ $n = 1$ composition

The (PDEA)PbI₄ composition was annealed at higher temperatures than PDMA-based compositions. The temperature, estimated by the pyrometer, and the GIWAXS patterns from the resulting films are displayed in Fig. 6.17. The sample 1 showed no high order reflections and its orientation was close to random (Fig. 6.16(c)), possibly due to the high temperature annealing. A slightly reduced temperature (sample 2) resulted in a thicker film, since high order reflections are visible in Fig. 6.17(b), and the appearance of preferred orientation at 75°, displayed in Fig. 6.16(c). Like in the iodide-based (PDMA)PbI₄ composition, the long axis of the unit cell c was slightly longer than in the case of a hotplate-annealed sample [178], possibly due to the differences in the annealing temperature and time, which resulted in a slightly different growth mechanism. A small difference in the unit cell parameter between the annealing methods in comparison to the case of PDMA-based compositions might originate from the internal properties of the PDEA spacer cation, which prefers to rather adapt the orientation between random and

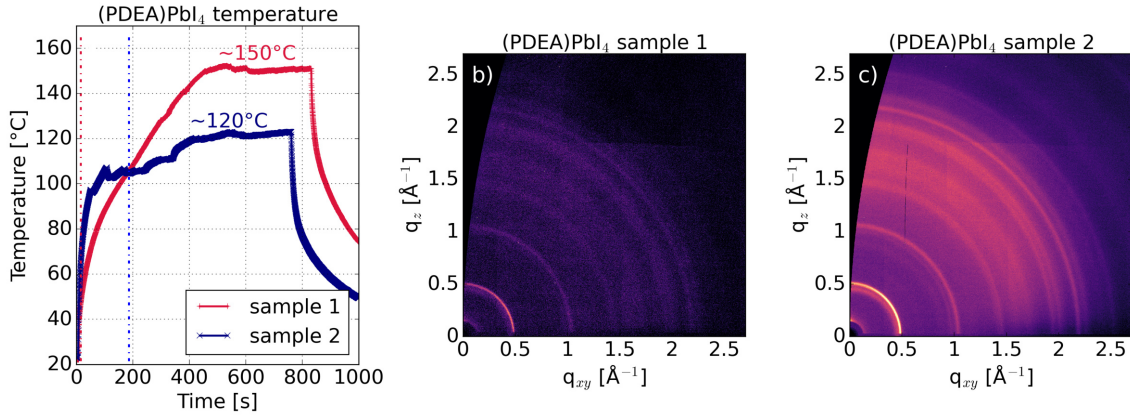


Figure 6.17.: GIWAXS reciprocal space maps of the PDEA-based DJ $n = 1$ 2D compositions deposited onto TiO_2 -coated glass at 0.2° angle of incidence showing structures within the sample after annealing: (a)(PDEA) PbI_4 sample 1 and (b)(PDEA) PbI_4 sample 2.

horizontal. (PDEA) PbI_4 composition does not show a preferred vertical orientation even after annealing on a hotplate [178], with the (100) reflection at $|q| = 0.5 \text{ \AA}^{-1}$ being the most intense in both current experiment (Fig. 6.17(b)) and published in literature [178].

6.4.3. Effects of halides and annealing rate on $\tilde{n} = 1$ DJ compositions

The studied compositions, based on PDMA and PDEA spacer cations, formed 2D DJ $n = 1$ phases, characterized by the presence of the characteristic (100) reflections. For the (PDMA) PbI_4 composition, variations in the annealing ramp and maximum temperature (Fig. 6.13) resulted in diverse preferred orientations of the $n = 1$ phase (Fig. 6.16(a)). Rapid annealing at high temperature led to the random orientation, whereas slower annealing at lower temperature resulted in the preferred vertical orientation. This can be explained by the growth mechanism: high temperature is able to partially decompose 2D organic-inorganic perovskite material, while optimal annealing parameters gently evaporate precursor solution and form a 2D perovskite with preferred vertical orientation.

The (PDMA) PbBr_4 composition exhibited the $n = 1$ phase prior to annealing, as the scattering signal from it can be seen in Fig. 6.15(c), mirroring the behavior of the 3D MAPbBr_3 perovskite composition which forms perovskite phase at room temperature after spin-coating [238]. The MAPbI_3 composition, in contrast, typically forms intermediate phases and requires thermal annealing. Similarly, (PDMA) PbI_4 also requires annealing to form an $n = 1$ 2D DJ phase. Their distinct formation mechanisms may be linked with dissimilarities in I- and Br-based parts of the composition, as it is also observed for mixed halide 3D perovskites. This might be the origin of the halide segregation under light illumination in the mixed halide 2D perovskite composition (PDMA) $\text{PbI}_{0.5}\text{Br}_{0.5}$, reported previously [180]. The resulting (PDMA) PbBr_4 film exhibited a preferred vertical orientation of the $n = 1$ phase (Fig. 6.12 and Fig. 6.16(a)), similarly to the (PDMA) PbI_4

composition. This might be connected with the ability of PDMA spacer cation to form $n = 1$ 2D DJ phase [178].

The (PDEA)PbI₄ composition was annealed at two temperatures, and, same as in the case of (PDMA)PbI₄, it influenced the appearance of the preferred orientation for $n = 1$ phase (Fig. 6.16(b)). For high temperature annealing (Fig. 6.17(a)), the resulting orientation was close to random, while low temperature annealing resulted in the formation of 2D $n = 1$ phase with its preferred orientation at 75°, which is in agreement with previously published results [178].

In addition, the PDEA-based samples exhibit a trend similar to that of the PDMA- and iodide-based samples: rapid annealing leads to a thinner film, while optimal annealing parameters do not cause material decomposition, resulting in a higher order of reflections (compare Fig. 6.17(b) and Fig. 6.17(c)).

In summary, the formation of the 2D DJ $n = 1$ phase is influenced by the halide component present in the composition, and can be achieved either before (bromide-based) or during (iodide-based) the annealing treatment. This might be the origin of the halide segregation mechanism in mixed halide compositions, based on PDMA spacer cation [180], since separate crystallization pathways for structures with different halides were observed in the case of 3D perovskites [39]. The estimated thickness of the final film and the orientation of the $n = 1$ phase are directly impacted by the annealing parameters. It has been observed that enhancing the temperature leads to random orientation and a decrease in film thickness. In contrast, optimal annealing parameters lead to the desired orientation, which is defined by the spacer cation, and a thicker film exhibiting higher order reflections.

6.5. Conclusions from this chapter

In present chapter, exemplary 2D perovskite compositions were studied during spin-coating and subsequent annealing. Depending on the spacer cation type, RP compositions based on monofunctional BNA and DJ compositions based on bifunctional PDMA and PDEA were studied.

The BNA-based compositions showed a clear dependence on the halide used: iodide led to the formation of multiple polymorphs throughout the annealing treatment, with one of them being the $n = 1$ phase, reported in the literature [150]. However, when the lamp was switched off, a cooling-induced relaxation took place, which resulted in shortening of the spacer cation and subsequent conversion into a thermally degraded phase, which was also observed for compositions with $\tilde{n} = 2-3$, and possibly comes from the instability of iodide-based compounds. In contrast, bromide-based $\tilde{n} = 1$ composition directly formed $n = 1$ phase prior to annealing, without any intermediate and thermally-degraded polymorphs. This might also be based on the effects of bromide, which forms the target perovskite phase prior to annealing in 3D compositions [39]. A common feature, observed for both BNA-based $n = 1$ compositions is the refraction effect [271], which originates

from the good condition of the surface, and can be observed between the critical angles of the deposited film and substrate materials. This might be one of the beneficial effects of BNA spacer cation, which was not observed previously. For compositions with $\tilde{n} = 2-3$, the layout of the formed phases almost did not change from the replacement of iodide with bromide, only for FA-based compositions the difference was observed. In particular, for the $\tilde{n} = 2$, in bromide addition suppressed the formation of $n = 2$ phase, since mostly $n = 1$ phase was formed on top of the film, while for the $\tilde{n} = 3$, the iodide-based composition formed a hexagonal FAPbI₃ phase on top of the sample, while not disturbing the other phases. This is a common tendency for FA-based 2D $\tilde{n} = 3$ perovskite compositions [76]. Another difference was connected with the orientation of the 2D phases: for iodide- and FA-based compositions, mixed or random orientation was observed, while for the bromide-based compositions, only out-of-plane orientation of the spacer cations was detected. The orientation of the formed 2D phases is beneficial for solar cells to be used as capping layers, since the orientation of the spacer cation is out-of-plane, while the resulting 3D perovskite phase is stabilized. Thin films, based on BNA spacer cation had thicknesses of ~ 30 nm, with the composition of $\tilde{n} = 1$ having the smallest roughness in comparison to the compositions with $\tilde{n} = 2-3$.

The studied DJ compositions, based on PDMA and PDEA spacer cations, formed $n = 1$ phases as expected [178]. However, additional insights into their formation were gained. In particular, iodide-based compositions required annealing treatment in order to complete the formation of the $n = 1$ phase, while PDMA and bromide-based composition formed the $n = 1$ phase already prior to annealing. This result is comparable with 3D iodide- and bromide-based compositions [39], and might reflect the origins of halide segregation under light illumination in the mixed 2D composition (PDMA)Pb(I_{0.5}Br_{0.5})₄, reported previously [180]. In addition to this essential observation, the annealing temperature seems to directly influence the orientation of the formed 2D perovskites and thin film thickness. In particular, high temperature annealing results in the random orientation of perovskites with PDMA or PDEA spacer cations, while the optimal annealing parameters result in a strong out of plane orientation (PDMA-based compositions) or a preferred orientation at 75°, closer to horizontal for (PDEA)PbI₄ composition, which could not be observed based only on *ex situ* GIWAXS data [178]. Based on XRR data, PDEA-based thin film with optimal annealing parameters exhibited a thickness of 30 nm, while having a higher roughness than film with RP phases. This reflects a clear influence of monofunctional and bifunctional spacer cations on thin film roughness. The additional knowledge on the studied DJ phases and their thermal sensitivity can be used for optimizing the annealing parameters during fabrication, thus achieving well-oriented 2D perovskites, based on hydrophobic spacer cations.

7. Conclusion and outlook

7.1. Summary and conclusion

Grazing incidence X-ray scattering experiments introduce certain limitations on the chambers which can be fixed on the diffractometer and built into the beamline infrastructure. In the current work, the experimental chamber for *in situ* grazing incidence wide-angle X-ray scattering during spin-coating at synchrotron facilities was developed, its sketch with all systems is presented in Fig. 7.1. The complete characterization of all systems within the chamber and assembly instruction is provided in Chap. 4. First of all, it features spinning with very low displacement values ($\sim 3\text{ }\mu\text{m}$), since the sample height is crucial for grazing incidence scattering experiments. An X-ray beam enters the sample at the low angle of incidence ($\alpha_i = 0\text{-}1^\circ$) and even small changes in the angle of incidence will result in changes of the X-ray beam penetration depth, which is crucial for thin film characterization. Secondly, the atmosphere within the chamber is controlled *via* utilizing humidity and oxygen sensors, placed at the sample height for more precise measurements. In order to speed up the crystallization of thin films by removing the excess solvent during thin film deposition, two additional methods, which can be applied during spin-coating, for achieving the supersaturated state are supported in the designed chamber: antisolvent-assisted treatment and gas quenching. Spin-coating procedure of perovskite materials often requires a post-treatment for triggering the conversion of solvent-based or solid intermediate phases into the target perovskite phase. A halogen lamp with the maximum power of 150 W directed to the sample table is utilized for sample annealing. Perovskite thin films, deposited from solution, often change their colors due to the transition from precursor phases into the perovskite phase, which also changes the optical properties. To visually inspect thin film transformation, a HQ PiCamera is mounted on a chamber flange and targeted at the sample table through the window. To characterize and track changes in the optical properties of the materials under study and estimate the thickness of the deposited thin film, a DRS system with a sensing area diameter of 1 mm is introduced into the chamber infrastructure.

Since scattering experiments which are using high brilliance sources are done inside of the experimental hutches, all systems within a sample environment have to be remotely controlled and accessed from the control hutch. This resulted in developing a code on Python, which was then transferred into TANGO platform, commonly used at synchrotron facilities. As a result, this chamber can be controlled from the control PC and

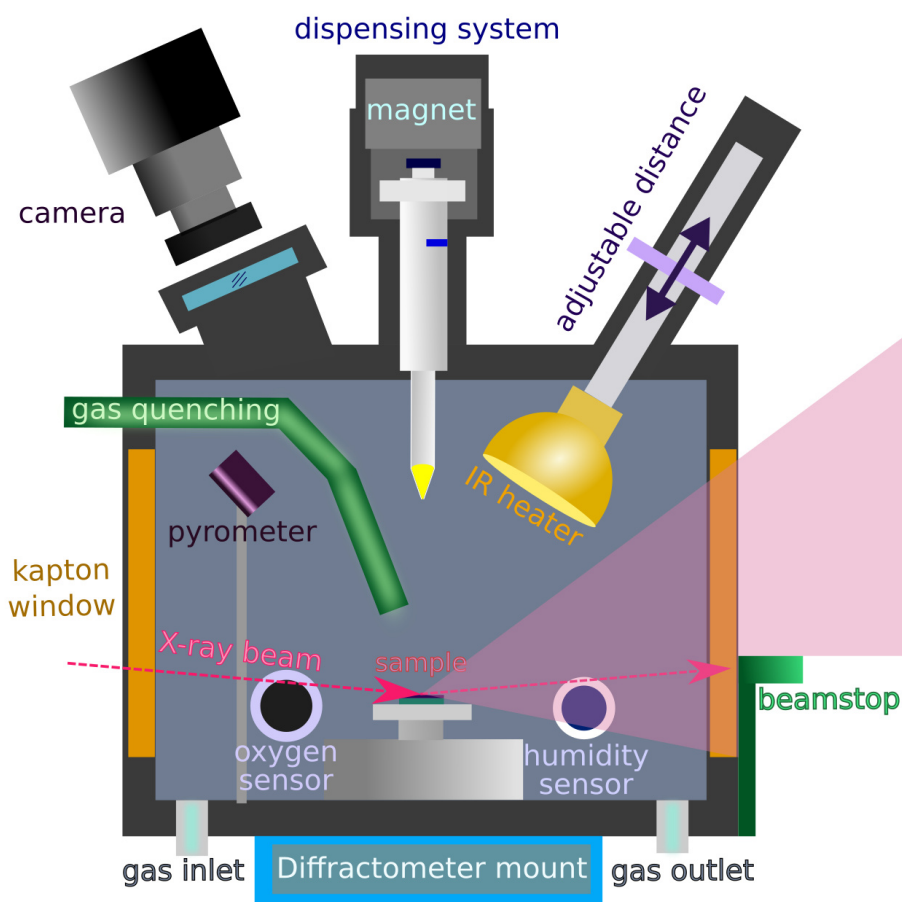


Figure 7.1.: One-step conversion method in the spin-coating chamber: 40-60 μL of the precursor solution is dropped onto a glass (bare or coated) substrate, spin-coated at 1000 rpm for 10 s, followed by spinning at a higher speed, typically 4000 rpm for 30 s. A halogen lamp is used to perform a subsequent heat treatment, resulting in the crystallization of the thin film.

can be easily synchronized with the beamline infrastructure.

The current work was focused on studying perovskite crystallization pathways depending on the deposition methods as well as their compositions. A brief summary table of the intermediate phases: solvent-based and solid structures, obtained during perovskite thin film growth are shown in Fig. 7.2 (single cations) and Fig. 7.3 (mixed cations). The pure MAPbI_3 composition forms a solvent-based complex, namely $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ [152], which converts into perovskite phase upon annealing. The FAPbI_3 composition, is able to form different solvent-based phases, depending on the precursor solution and deposition method: for the pure DMF solvent only DMF-based intermediate phases were observed [147, 148], while for the (4:1) DMF:DMSO precursor solution and IPA antisolvent, a $\text{FAI} \cdot \text{PbI}_2 \cdot x\text{DMSO}$ [38] templating structure was identified. If solvent complexes are present, they tend to convert into the non-perovskite 2H hexagonal phase, which turns into the target perovskite structure upon annealing. The MAPbBr_3 composition directly

Composition	One step conversion (anneal)	One step conversion (spin & anneal)	Antisolvent	Gas-quenching
MAPbI ₃	(MA) ₂ Pb ₃ I ₈ ·2DMSO	(MA) ₂ Pb ₃ I ₈ ·2DMSO	IPA intermediate, (MA) ₂ Pb ₃ I ₈ ·2DMSO	(MA) ₂ Pb ₃ I ₈ ·2DMSO
FAPbI ₃	FAPbI ₃ ·DMF, 2H	2H	FAI-PbI ₂ ·xDMSO, 2H	2H
FAPbI ₃ in DMF	-	(FA) ₂ Pb ₃ I ₈ ·4DMF, FAPbI ₃ ·2DMF, FAPbI ₃ ·DMF, 2H	(FA) ₂ Pb ₃ I ₈ ·4DMF, FAPbI ₃ ·2DMF, FAPbI ₃ ·DMF, 2H	(FA) ₂ Pb ₃ I ₈ ·4DMF, FAPbI ₃ ·2DMF, 2H
MAPbBr ₃	perovskite	perovskite	perovskite	-
CsPbI ₃	δ-CsPbI ₃	-	-	-

Figure 7.2.: List of intermediate phases between precursor solution and final perovskite films for single cation compositions obtained by different methods. Colors represent corresponding phases, which are also marked in the data analysis. One step conversion data (anneal) is shown in Sec. 5.2. One step conversion data (spin & anneal) is shown in Sec. 5.5. Antisolvent-assisted data is shown in Sec. 5.6. Gas quenching data is shown in Sec. 5.8. FAPbI₃ in DMF is shown in Sec. 5.4 as an additional research on DMF-based intermediate phases.

adapts cubic perovskite phase at room temperature, while the annealing treatment leads to the increased size of crystallites.

For the mixed cation FA:MA composition, three hexagonal polymorphs were observed: 2H, 4H and 6H, while the formation of solvent-based intermediate phases depends on the deposition method. For both FA:MA:Cs and FA:MA:Cs:Rb compositions, the 4H hexagonal polymorph was found to be a dominant solid non-perovskite phase, which is in line with DFT calculations [227].

The addition of 5% CsI into single cation compositions partially suppressed the formation of solvent-based intermediate phases, while the antisolvent application improved the coverage of MAPbI₃ and MAPbBr₃ compositions. For the FAPbI₃ composition, IPA antisolvent application resulted in the direct formation of non-perovskite mixed cation hexagonal phase, which, due to the presence of Cs cations, had an increased temperature of conversion into the perovskite phase.

The summary on the orientations of $n = 1$ and $n = 2$ phases within two dimensional perovskite compositions based on monofunctional (BNA) and bifunctional (PDMA and PDEA) spacer cations is presented in Fig. 7.4. The compositions with preferred vertical orientation of the spacer cation can be optimally used as capping layers for 3D perovskite films, which then increases the environmental stability. The 2D perovskites with BNA as a spacer cation and $\tilde{n} = 1$ showed a clear dependence on the halide: iodide-based compo-

sition showed a formation *via* various polymorphs on the way to the target $n = 1$ phase, while after annealing relaxation of the 2D phase takes place, resulting in its conversion into a polymorph with a shorter out-of-plane parameter. For bromide-based $\tilde{n} = 1$ composition, $n = 1$ phase forms directly during spin-coating, and its degree of orientation does not significantly change during annealing treatment. Additionally, both of the BNA $\tilde{n} = 1$ compositions show a refraction effect, which suggests the high surface quality of the deposited thin films. For compositions with $\tilde{n} = 2-3$, no strong influence of halides on the phase composition was observed, only FA-based sample with iodide and $\tilde{n} = 3$ had additionally 2H FAPbI₃ phase, while FA-based sample with bromide and $\tilde{n} = 2$ did not form an $n = 2$ phase, which might be due to the dominant role of $n = 1$ phase in FA-based compositions, as $n = 2$ phase could only form between the $n = 1$ and cubic perovskite phases.

DJ 2D perovskite compositions based on PDMA showed the following feature: under rapid annealing at high temperature, the orientation of the $n = 1$ for iodine-based composition was found to be random, while the optimal slow annealing at low temperature resulted in a desired vertical orientation of the spacer cation. The other distinguishable result for the PDMA spacer cation arises from the diversity of halides: the iodine-based composition converted into $n = 1$ phase only upon annealing, while bromine-based composition formed the $n = 1$ phase prior to annealing. This mechanism might be a hint towards resolving the mystery of halide segregation in the PDMA-based mixed halide samples, reported recently [180]. For the PDEA-based composition, a more random orientation of the $n = 1$ phase was observed, which supports the previously published data [178].

Current work includes mainly unpublished data, while the developed spin-coating chamber provided an opportunity to study the effects of antisolvent application on triple-cation perovskite deposition [38] and track the growth mechanisms of mixed-halide perovskite compositions, which exhibit halide segregation under light illumination [39].

The designed chamber with low "wobbling" amplitude of the spinning sample table and reliably integrated parts gives a great opportunity to explore a wide variety of different materials. *In situ* GIWAXS during spin-coating is a powerful tool which gives important insights into thin film crystallization kinetics, which can be used for fine adjustment of both the precursor solution (solvents, cations, halides) and deposition method. The increasing amounts of scattering data, produced at synchrotron facilities, can be processed using machine learning tools [37], which will lead to essential improvement of thin film fabrication based on the analysis on the flight, resulting in a rapid optimization procedure of material deposition.

7.2. Outlook

Since the developed spin-coating chamber is only a beginning of the journey of studying crystallization kinetics of different materials, it would be essential to carry out extensive

Composition	One step conversion (anneal)	One step conversion (spin & anneal)	Antisolvent	Gas-quenching
FA:MA	(MA) ₂ Pb ₃ I ₈ ·2DMSO, DMF-based, 2H, 4H, 6H	4H, 6H	FAI-PbI ₂ ·xDMSO, DMF-based, (MA) ₂ Pb ₃ I ₈ ·2DMSO, 2H, 4H, 6H	2H, 4H, 6H
FA:MA:Cs	(MA) ₂ Pb ₃ I ₈ ·2DMSO, 4H	4H	FAI-PbI ₂ ·xDMSO, (MA) ₂ Pb ₃ I ₈ ·2DMSO, 4H, δ -CsPbI ₃	4H
FA:MA:Cs:Rb	δ -CsPbI ₃ , 4H	-	-	-
(MAPbI ₃) _{0.95} (CsI) _{0.05}	-	(MA) ₂ Pb ₃ I ₈ ·2DMSO	(MA) ₂ Pb ₃ I ₈ ·2DMSO	-
(FAPbI ₃) _{0.95} (CsI) _{0.05}	-	2H	IPA intermediate, FAI-PbI ₂ ·xDMSO, 2H	-
(MAPbBr ₃) _{0.95} (CsI) _{0.05}	-	perovskite	perovskite	-

Figure 7.3.: List of intermediate phases between precursor solution and final perovskite films for mixed cation compositions obtained by different methods. Colors represent corresponding phases, which are also marked in the data analysis. One step conversion data (anneal) is shown in Sec. 5.2. One step conversion data (spin & anneal) is shown in Sec. 5.5 and Sec. 5.7. Antisolvent-assisted data is shown in Sec. 5.6 and Sec. 5.7. Gas quenching data is shown in Sec. 5.8.

research on combining X-ray scattering methods and measuring the optical properties of the thin films prepared. This can be done by using the implemented DRS probe as well as adapt other techniques for thin film characterization. In particular, it might be interesting to study the influence of the capping layers, which are, for example, based on 2D perovskites, on top of the prepared 3D perovskite films. Another beneficial characterization can be made by studying *in situ* the formation mechanisms of mixed cation 3D perovskite compositions through different hexagonal phases with varying percentage of inorganic cations [138] and combining this research with tracking optical properties by DRS.

Fabrication of 2D perovskite thin films is typically done with default parameters; however, it can be further improved by optimizing the growth kinetics depending on the annealing profile. This kind of analysis could be done on-the-flight during the beam-time, since one can prepare to track specific Bragg peaks from the desired 2D phases and avoid the formation of phases with shorter out-of-plane lattice parameters. 2D perovskite compositions require careful handling and non-destructive annealing, which can be done by reducing the maximum temperature and tracking the preferred orientation of the 2D phases formed: optimal annealing parameters sometimes result in a strong vertical orientation of the spacer cations, while extensive annealing can lead to the formation of the 2D phase with randomly oriented spacer cations.

Spacer cation	Halide	n = 1 composition	Central cation	n = 2 composition		n = 3 composition	
				n = 1 phase	n = 2 phase	n = 1 phase	n = 2 phase
BNA	Iodide		MA				
			FA				
	Bromide		MA				
			FA		--		
PDMA	Iodide		• n = 1 phase in n=1 BNA compositions has an out-of-plane orientation • Using MA as a central cation and I as a halide results in out-of-plane orientation of n=1 and n=2 phases • Using FA as a central cation and I as a halide results in mixed orientations of both n=1 and n=2 phases and the appearance of random orientation • Using Br as a halide results in out-of-plane orientation of both n=1 and n=2 phases				
	Bromide						
PDEA	Iodide						

Figure 7.4.: Summary on the preferred orientations of the observed phases within different compositions: RP phases (BNA spacer cation) on ITO-coated substrates and DJ phases (PDMA and PDEA spacer cation) on TiO₂-coated substrates.

The increasing amount of X-ray scattering data has led to the application of machine learning methods for their analysis [273–276]. Recently, a machine learning-based fast processing of the quick ($\sim$ millisecond resolution) XRR measurements during spin-coating was developed as a tool for analyzing surface morphology and thin film structure[277]. Since *in situ* GIWAXS experiments generate a large amount of data that must be analyzed, the designed chamber can be used in combination with deep learning-based feature detection [37] which is capable of identifying crystal structures from Bragg peaks on the fly during thin film crystallization. It allows adjusting and optimizing the annealing parameters in case of incomplete conversion of the intermediate phases into the expected crystal structure. Apart from that, preliminary analysis already during data acquisition allows one to classify the resulting samples and makes the post-processing simpler.

Part III.

Appendix

A. Additional figures for Chapter 4

This chapter contains additional figures for Chap. 4. In particular, in Fig. A.1 a photo of the chamber in operation at P08 beamline at DESY for antisolvent-assisted deposition is presented. The variability of absorbance spectra of bare FTO substrates and FTO substrates with perovskite precursor is presented in Fig. A.2, which is in particular important for infrared annealing done by a halogen lamp. Tab. A.1 shows a list of annealing systems used during *in situ* GIWAXS measurements with key parameters and details. A 3D representation of the designed DRS probe holder is displayed in Fig. A.3. Thin film thicknesses, estimated from DRS measurements for different final spinning speeds of the spin-coater during deposition, are presented in Fig. A.4. An exemplary perovskite thin film fabrication, done by gas quenching route and recorded with PiCamera, showing the conversion from liquid phase to solid phase with thin film color change, is presented in Fig. A.5. The experimental geometry, used for estimation of the sample table "wobbling" during spin-coating is presented in Fig. A.6. Fig. A.7 shows an internal memory layout of the used thermopile array HTPA80x64d from Heimann, which includes parameters and data, required for compensation and correction of the internal and external deviations.

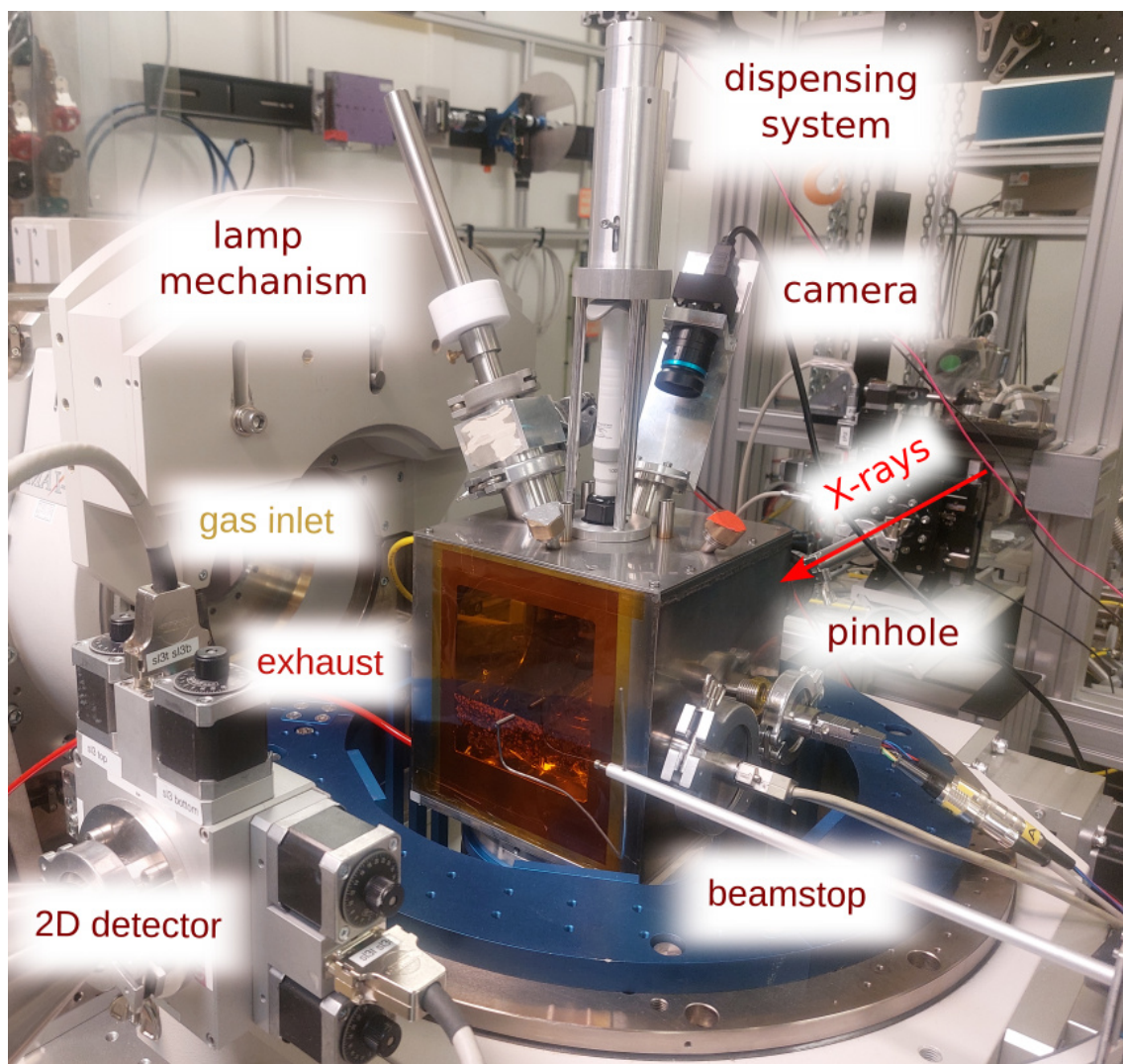


Figure A.1.: Spin-coating chamber for *in situ* GIWAXS measurements, a photo of the chamber in operation at beamline P08 [181] at DESY, a setup for one step conversion or antisolvent-assisted fabrication method.

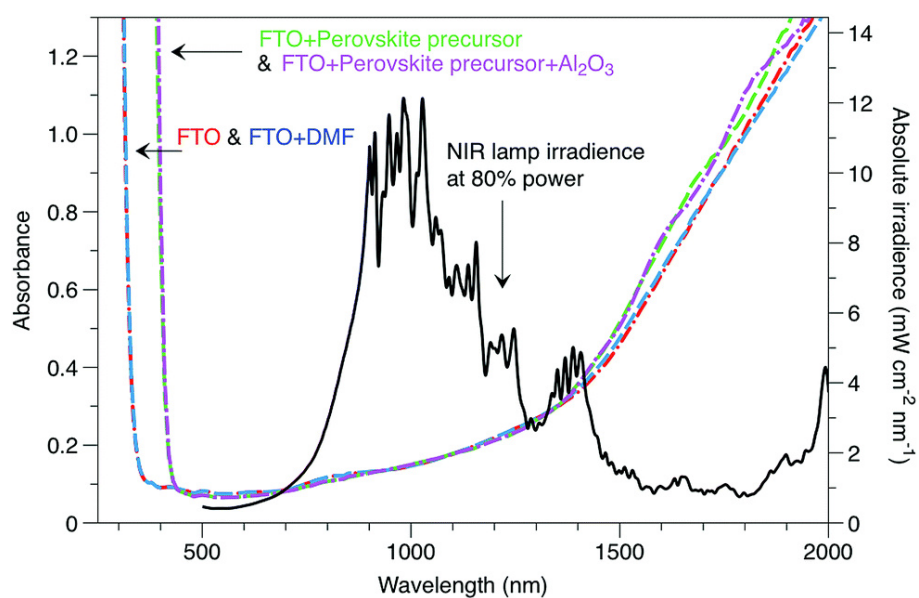


Figure A.2.: Absorbance spectra for perovskite precursor solutions and FTO-coated glass substrates, as well as irradiance spectra for a NIR lamp at 80% power. Source: [201].

Table A.1.: List of annealing systems used during *in situ* GIWAXS measurements at different synchrotron facilities with key parameters: annealing type, details and results.

Material	Annealing type	Details & Results	Source
$\text{Bi}_2\text{O}_3\text{-SiO}_2$	Rapid thermal processing (RTP)	two 120 mm long tungsten halogen lamps, annealing temperatures up to 1200°C	[200]
MAPbI_3	NIR annealing	Adphos Coil Lab LV2, tungsten filament halogen lamps with an output spectrum in the region of 250–2500 nm, peaking between 800 and 1200 nm	[201]
MAPbI_3 , $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_{1.5}\text{Br}_{1.5}$, $\text{CsPbI}_{1.5}\text{Br}_{1.5}$	Flash infrared annealing (FIRA)	The oven includes an array of NIR halogen lamps providing an illumination power of 3000 kW/m. The infrared pulse time drives the crystallization of perovskite films to obtain the suitable crystal morphology	[202]
MAPbI_3 , $\text{Cs}_{0.5}\text{MA}_{0.5}\text{PbI}_{1.5}\text{Br}_{1.5}$, $\text{CsPbI}_{1.5}\text{Br}_{1.5}$	FIRA	System is based on six near-infrared halogen lamp with peak emission at 1073 nm. The chamber temperature increased up to 600°C, while perovskite thin film temperature did not exceed 100°C.	[278]
MAPbI_3 with MACl additive	FIRA	The heater is composed of two 600 W infrared halogen lamps (Heraeus Noblelight), temperatures up to 210°C can be achieved. A stable perovskite phase was observed at ITO-coated substrate temperatures of 90°C up to 170°C.	[32]
MAPbI_3	NIR	Halogen lamp 64635 HLX from OSRAM [206] with maximum emissive energy at $\lambda = 905.6\text{ nm}$, temperatures above 200°C can be achieved.	this work

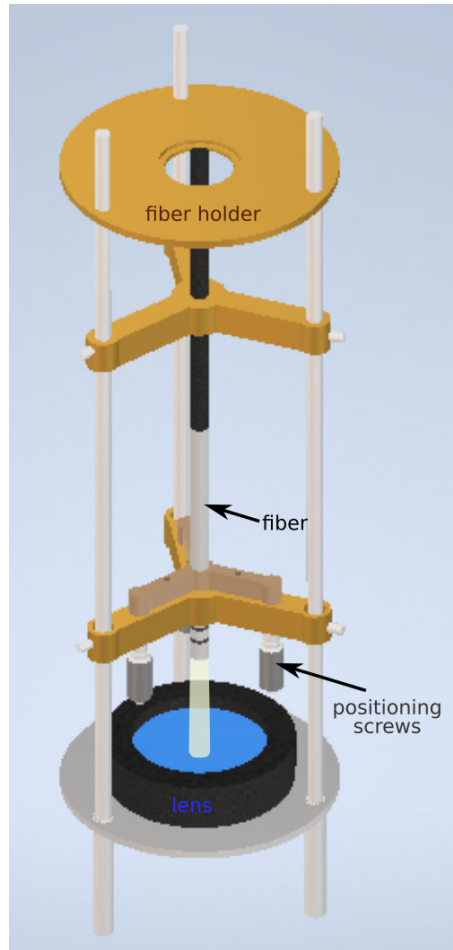


Figure A.3.: 3D technical drawing of a fiber holder for DRS fiber with a lens and positioning screws for fine adjustment, imported from Autodesk Inventor 2020 Certified Professional.

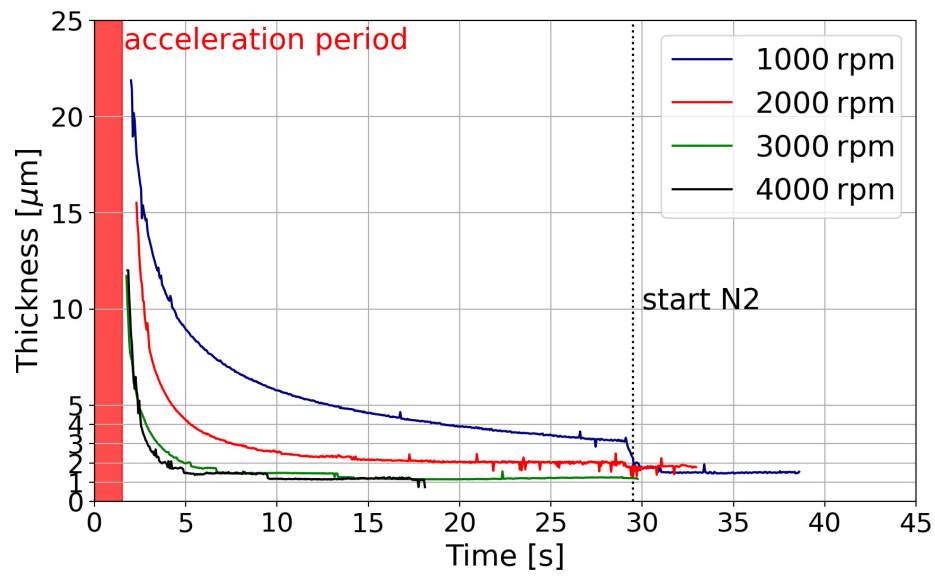


Figure A.4.: Thickness calculated from DRS data during the spin-coating process. The motor was started at 0 s but takes 2-3 s to get to the desired rotation speed. Nitrogen flow is started shortly before 30 s. Source: [213].

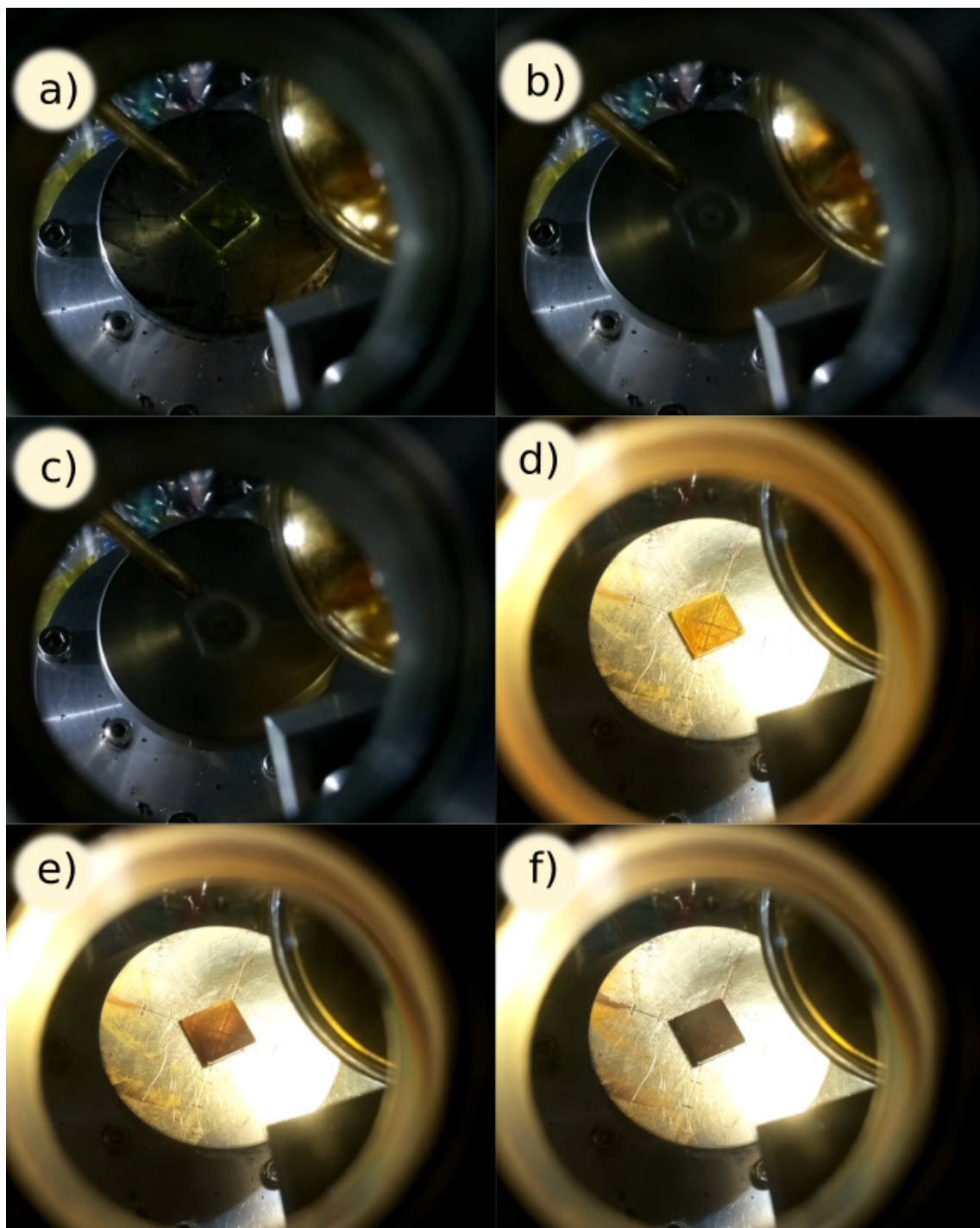


Figure A.5.: Perovskite thin film fabrication by gas quenching route recorded by PiCamera: a) deposited solution on the substrate; b) sample spinning; c) nitrogen gas jet on; d) annealing started; e) conversion started; f) conversion completed.

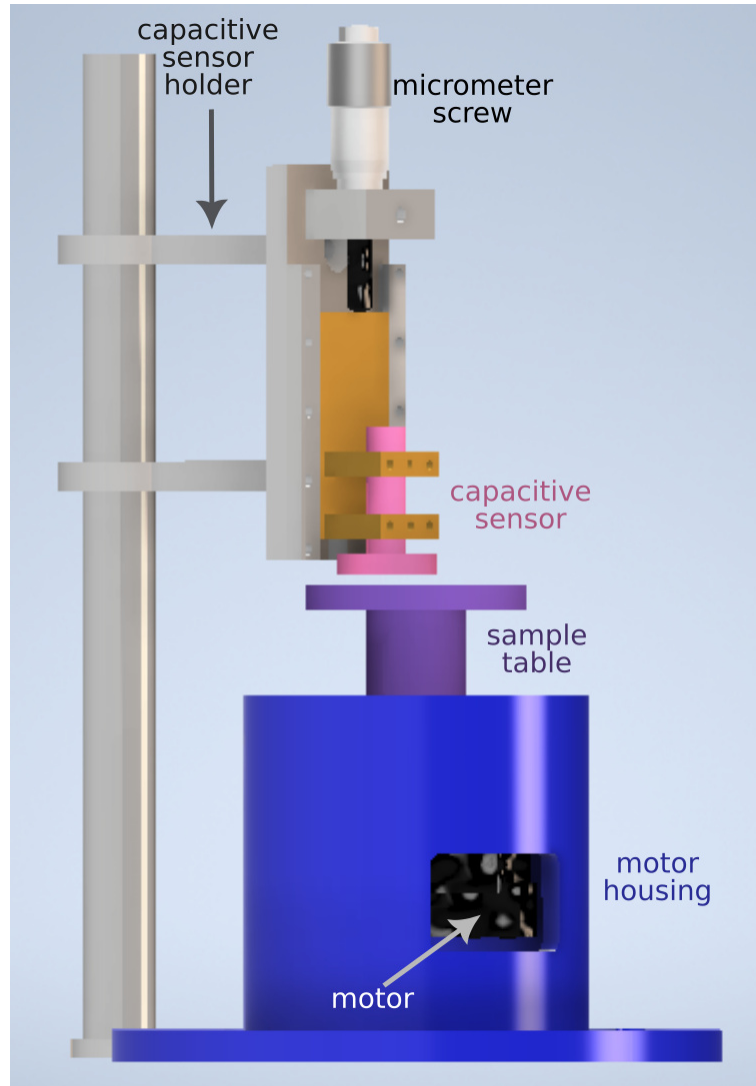


Figure A.6.: An experimental geometry for "wobbling" estimation of the sample table during spinning. Capacitive sensor is precisely positioned by a micrometer screw close to the sample table.

80x64d	0x00	0x01	0x02	0x03	0x04	0x05	0x06	0x07	0x08	0x09	0x0A	0x0B	0x0C	0x0D	0x0E	0x0F
0x0000	PixCmn [float]		PixCmax [float]		gradScale		MBIT(calib)		BIAS(calib)		CLK(calib)		epsilon		PU(calib)	
0x0010	Arraytype		VDDTH1		VDDTH2		PTAT-gradient (float)		PTAT-offset (float)		PTAT (Th1)		PTAT (Th2)		VddScOff	
0x0020																
0x0030																
0x0040																
0x0050																
0x0060	MBIT(user)		BIAS(user)		CLK(user)		BPA(user)		GlobalGain		GlobalOff		PU(user)			
0x0070																
0x0080																
0x0090																
0x00A0																
0x00B0																
0x00C0																
...																
...																
0x0800																
...																
0x11F0																
0x1200																
...																
0x1BF0																
0x1C00																
...																
0x2FF0																
0x3000																
...																
0x57F0																
0x5800																
...																
0x7FF0																

Figure A.7.: EEPROM (internal memory) overview of the HTPA80x64d from Heimann.

B. Additional figures for Chapter 5

This chapter contains additional figures for Chap. 5, which reflects the phase distribution within the studied perovskite compositions. The results of the GIWAXS patterns analysis before and after annealing are displayed in Fig. B.1. The initial scattering data, used for perovskite phase characterization (lattice constant and coherently scattering domain size) within final films (Fig. 5.8), is presented in Fig. B.2. The GIWAXS data in waterfall plots, presented in all other figures reflects the complexity of the phases, appearing within various perovskite compositions. The additional research on DMF-based intermediate phases, discussed in Sec. 5.4 with raw GIWAXS data presented in the current chapter highlights an interplay between intermediate phases depending on the deposition method.

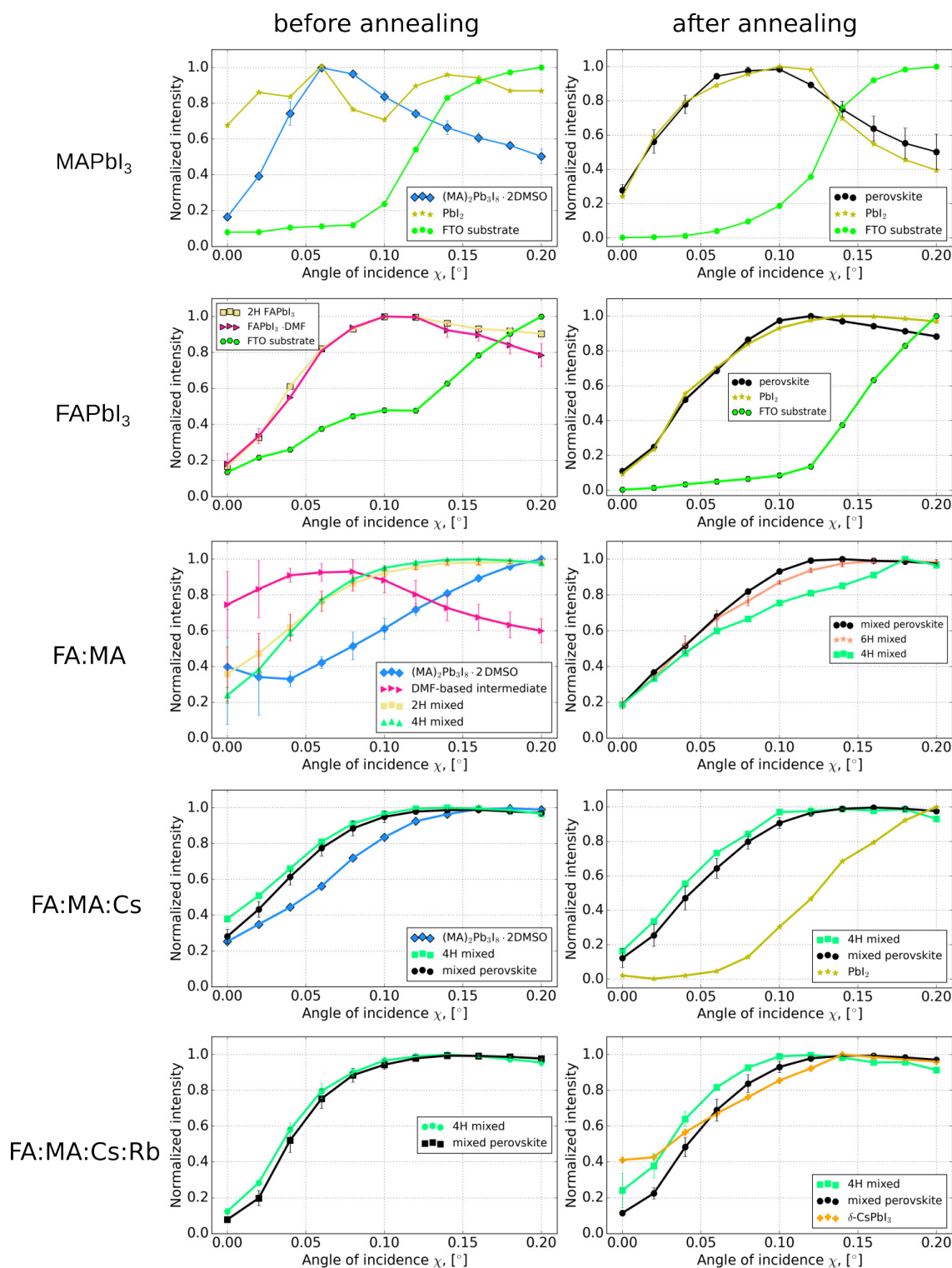


Figure B.1.: Intensity angular profiles of the structures within samples measured by GI-WAXS before and after annealing. Error bars were calculated by averaging over different reflections and samples.

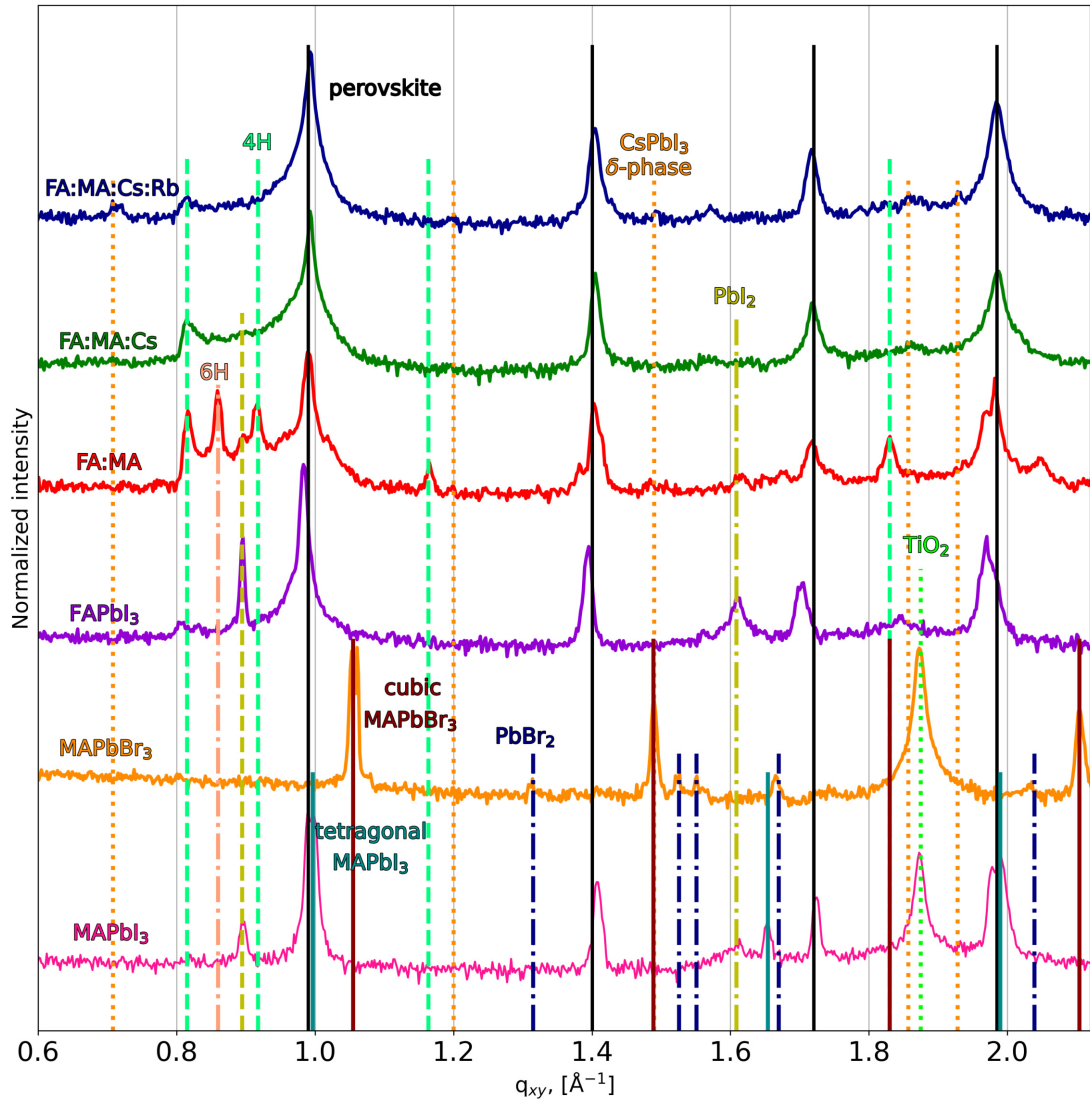


Figure B.2.: GIXD intensity profiles of all samples after annealing with marked structures.

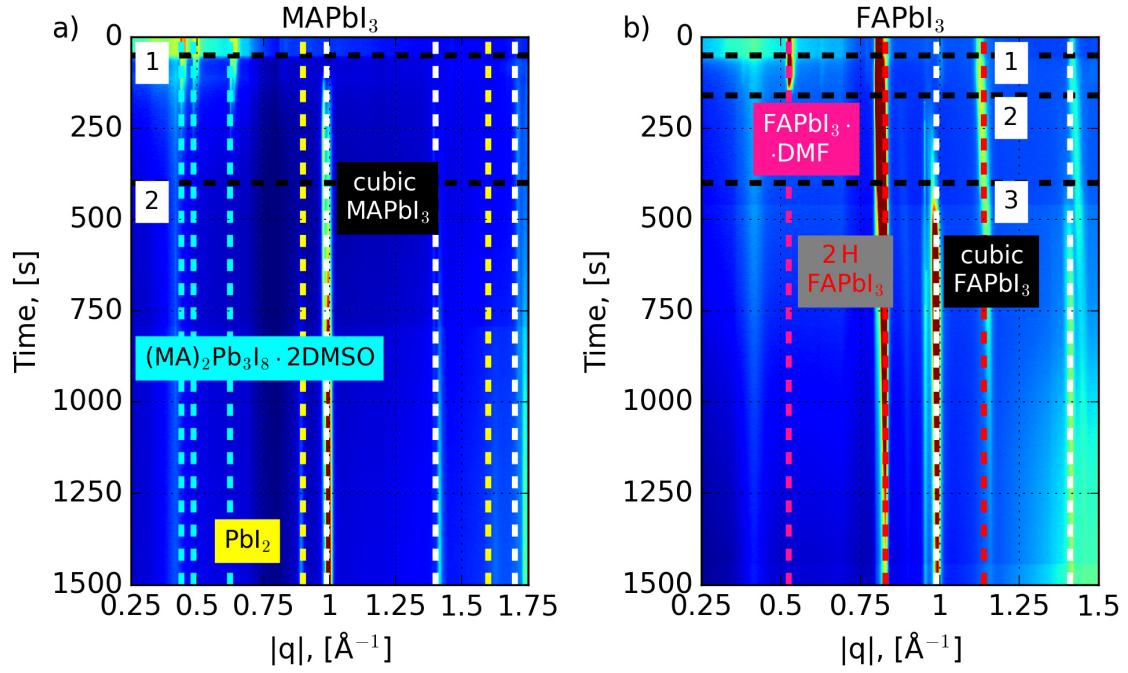


Figure B.3.: Azimuthally integrated synchrotron-based GIWAXS patterns of (a) MAPbI₃ and (b) FAPbI₃ compositions in waterfall plots, displaying the scattering intensity evolution. Horizontal lines indicate: 1 - beginning of the annealing experiment, 2 - end of (MA)₂Pb₃I₈·2DMSO intermediate phase conversion.

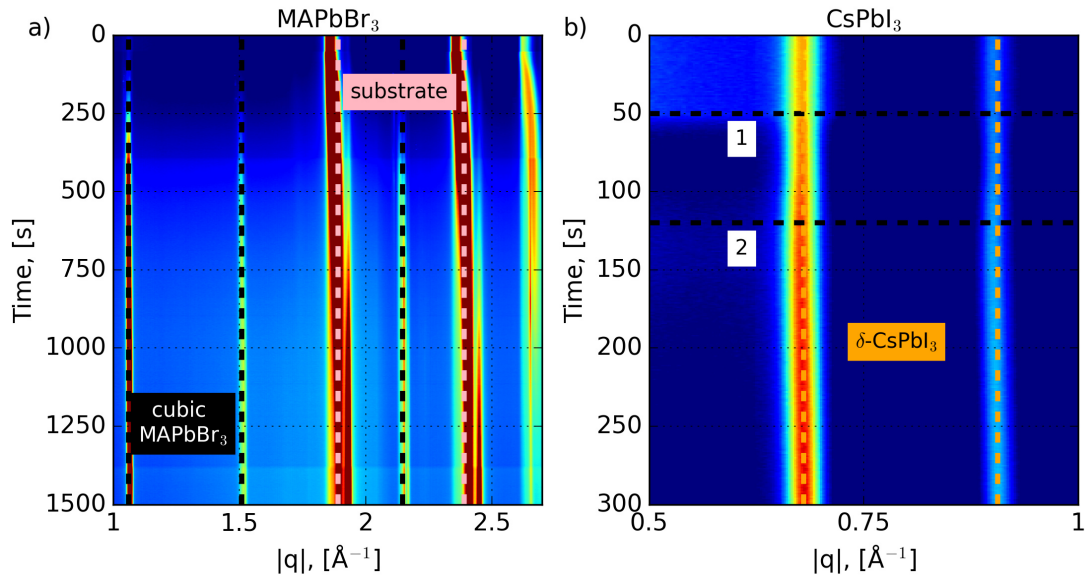


Figure B.4.: Azimuthally integrated synchrotron-based GIWAXS patterns of (a) MAPbBr₃ and (b) CsPbI₃ samples in waterfall plots, displaying the scattering intensity evolution. In (b) 1 - beginning of the annealing experiment, 2 - end of the first crystallization step.

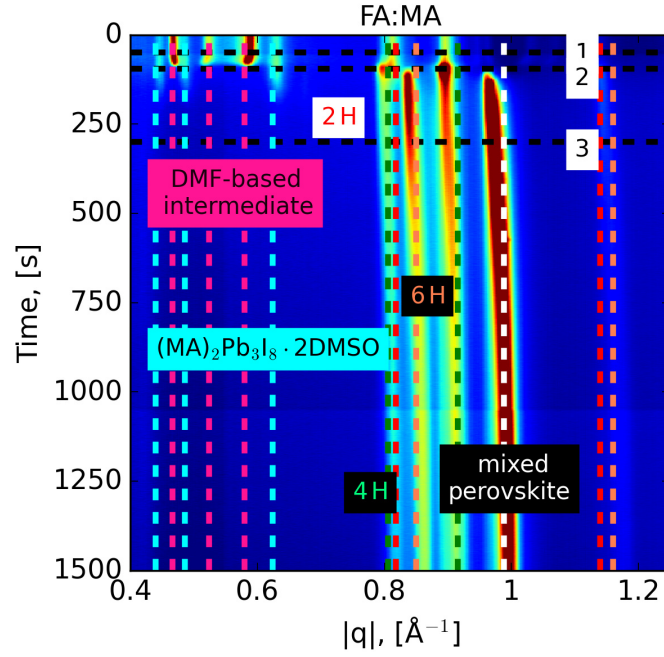


Figure B.5.: Azimuthally integrated synchrotron-based GIWAXS patterns of FA:MA sample in waterfall plots, displaying the scattering intensity evolution. Horizontal lines indicate: 1 - beginning of the annealing experiment; 2 - end of DMF-based intermediate phase conversion, pink region shows its duration; 3 - end of $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ intermediate phase conversion.

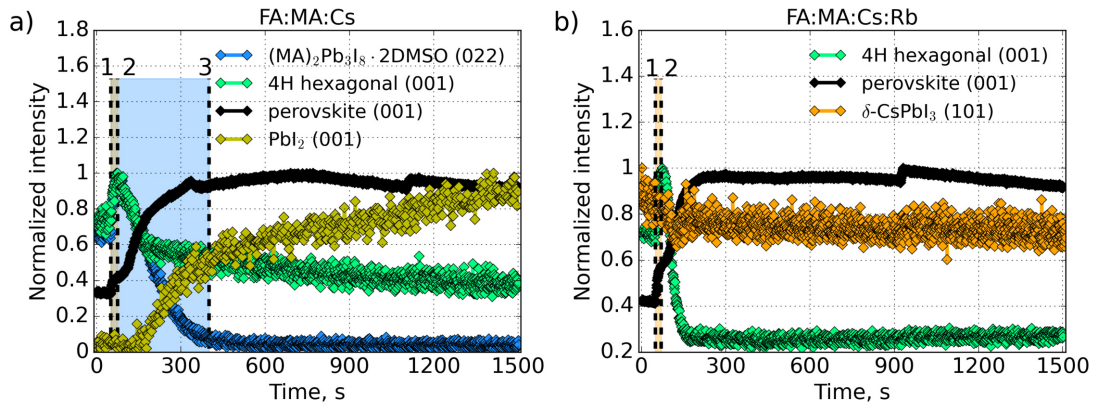


Figure B.6.: Integrated scattering intensities of the structures during crystallization of mixed-cation compositions: (a) FA:MA:Cs and (b) FA:MA:Cs:Rb: 1 - beginning of the annealing experiment, 2 - end of the first crystallization step in the mixed sample, orange region shows its duration, 3 - end of $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ intermediate phase conversion, blue region shows its duration.

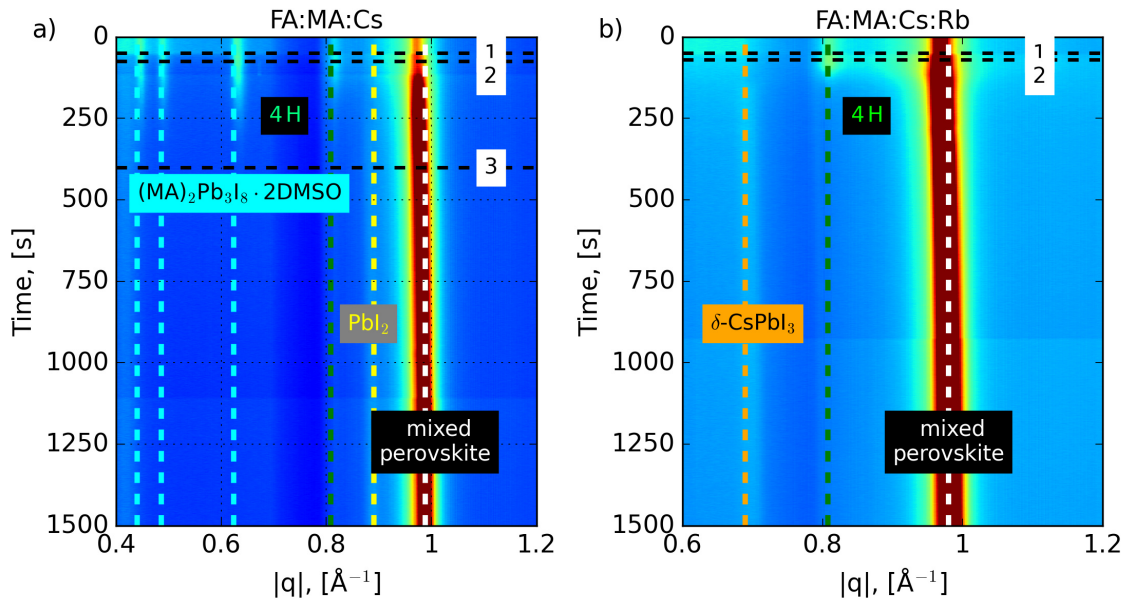


Figure B.7.: Azimuthally integrated synchrotron-based GIWAXS patterns of (a) FA:MA:Cs and (b) FA:MA:Cs:Rb compositions in waterfall plots, displaying the scattering intensity evolution. Horizontal lines indicate: 1 - beginning of the annealing experiment, 2 - end of the first crystallization step, 3 - end of $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ intermediate phase conversion.

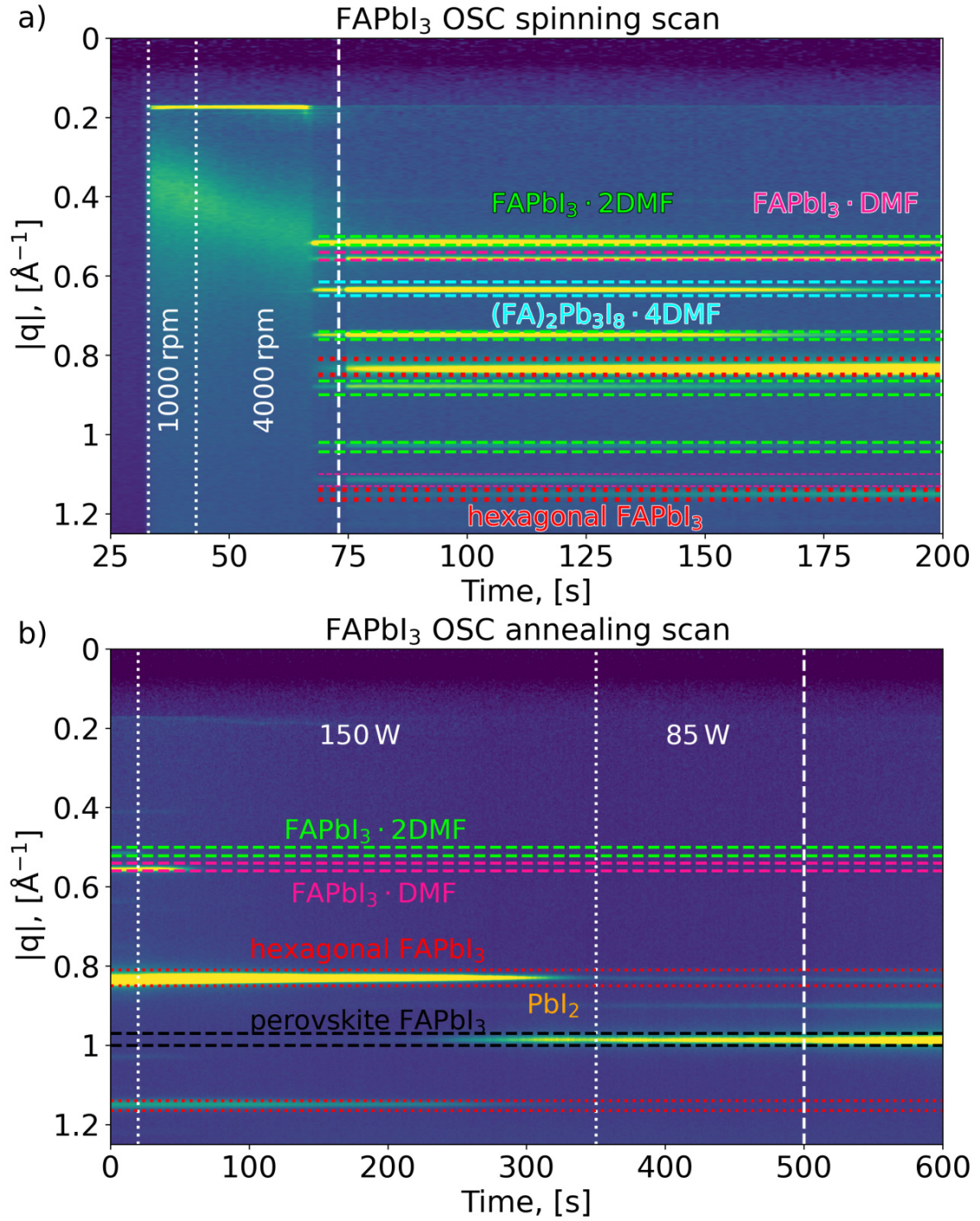


Figure B.8.: Azimuthally integrated synchrotron-based GIWAXS patterns of FAPbI₃ composition (pure DMF solvent) deposited by one step conversion method in waterfall plots with marked structures during (a) spinning and (b) annealing, displaying the scattering intensity evolution. Vertical lines indicate: (a) dotted - setting spinning speed to 1000 rpm and 4000 rpm, the dashed line indicated the end of spinning; (b) dotted - setting halogen lamp power of 150 W followed by 85 W, the dashed line indicated the end of annealing.

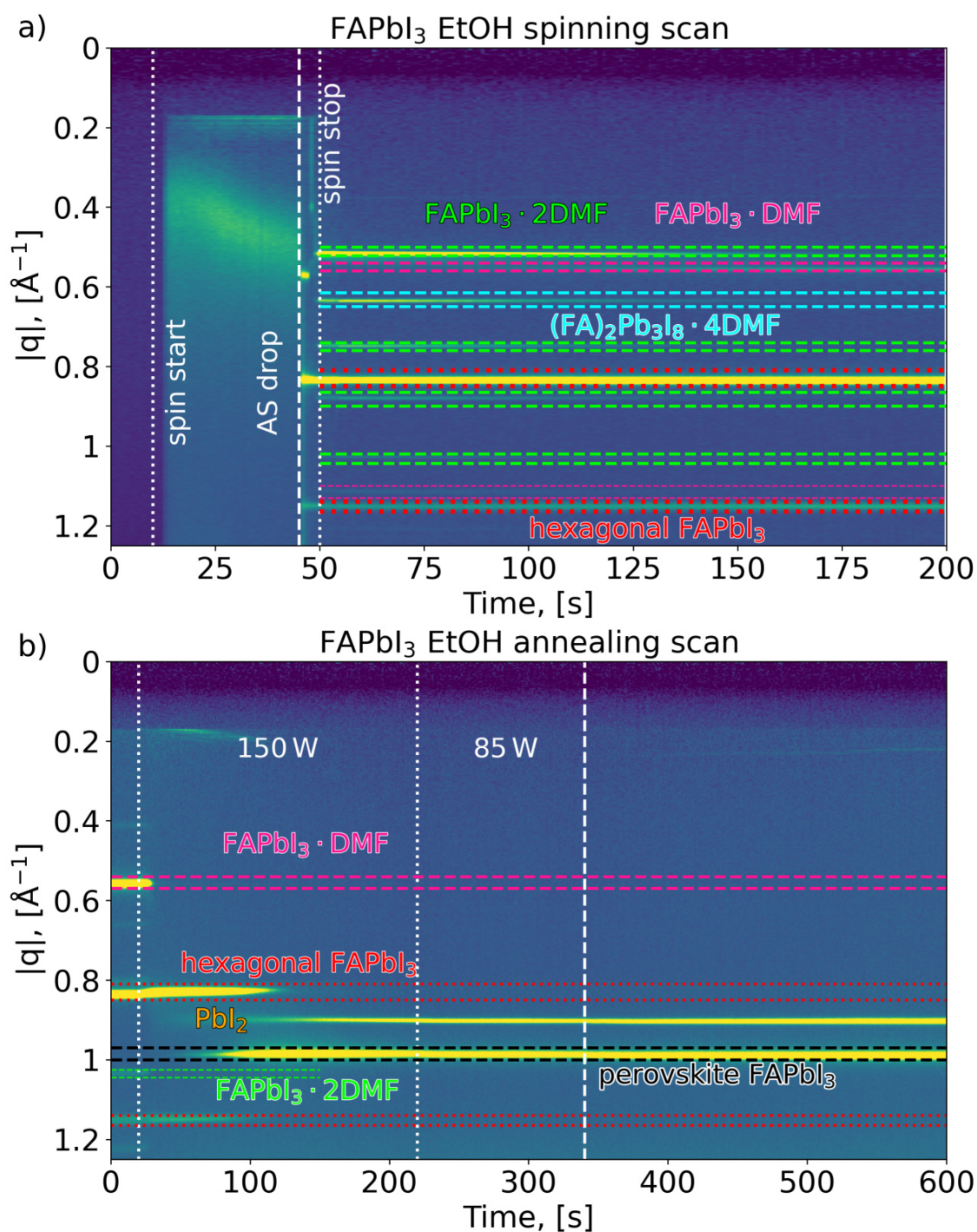


Figure B.9.: Azimuthally integrated synchrotron-based GIWAXS patterns of FAPbI₃ composition (pure DMF solvent) deposited by antisolvent-assisted method (EtOH) in waterfall plots with marked structures during (a) spinning and (b) annealing, displaying the scattering intensity evolution. Vertical lines indicate: (a) dotted - start spinning and end spinning, the dashed line indicated ethanol antisolvent application; (b) dotted - setting halogen lamp power of 150 W followed by 85 W, the dashed line indicated the end of annealing.

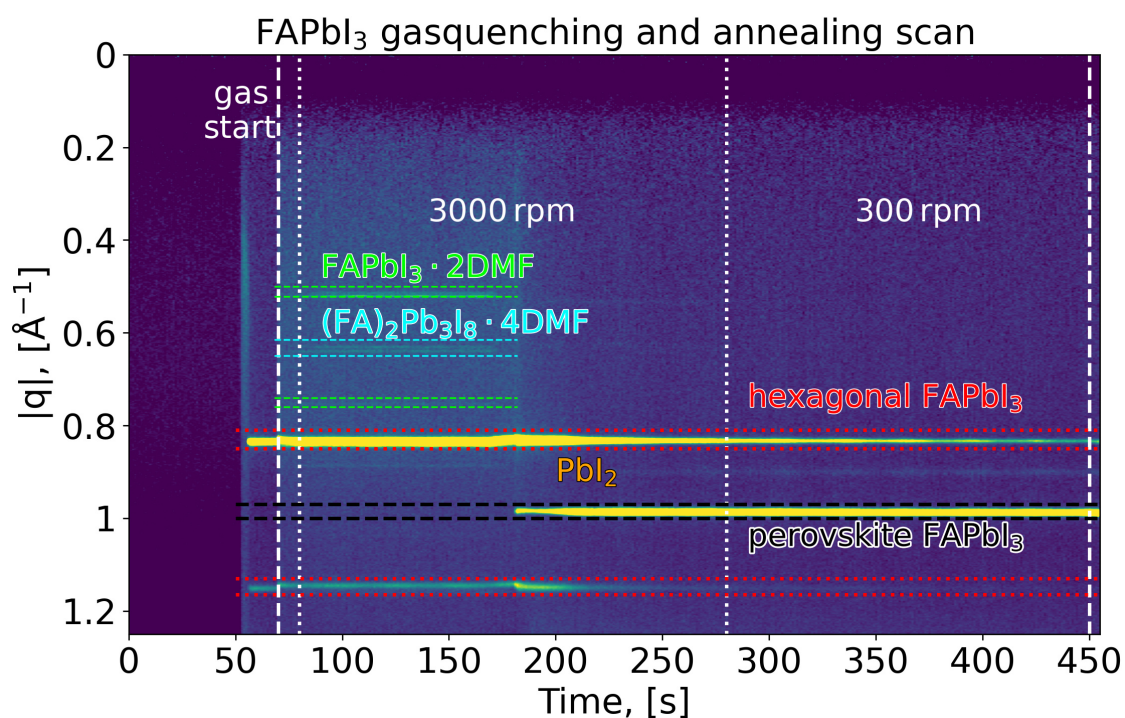


Figure B.10.: Azimuthally integrated synchrotron-based GIWAXS patterns of FAPbI₃ composition (pure DMF solvent) deposited by gasquenching-assisted method (EtOH) in waterfall plot with marked structures during simultaneous spinning and annealing (lamp power 90 W), displaying the scattering intensity evolution. Vertical lines indicate: dashed - beginning and end of the nitrogen stream supply, dotted - start spinning at 3000 rpm and 300 rpm, respectively.

C. Additional figures for Chapter 6

This chapter contains additional figures for Chap. 6. GIWAXS patterns, indicating refraction effect [271], observed for $(\text{BNA})_2\text{PbI}_4$ composition, are presented in Fig. C.1. Positions of Bragg peaks and refraction effect peaks for $(\text{BNA})_2\text{PbI}_4$ and $(\text{BNA})_2\text{PbBr}_4$ compositions for angles of incidence between 0.08° and 0.18° (critical angles of 2D perovskite phase and ITO-coating, respectively) are presented in Fig. C.2. A comparison between annealing-induced degradation of $(\text{BNA})_2\text{PbI}_4$, performed by hotplate annealing of the final film at 90°C for 5 days and *in situ* GIWAXS during and after annealing of the film by a halogen lamp is displayed in Fig. C.3. Degrees of orientation of $n = 1$ phases and $n = 2$ phases in BNA-iodide based compositions are shown in Fig. C.4 and Fig. C.5, respectively. The orientation profiles of the $n = 1$ phase in $(\text{BNA})_2\text{PbBr}_4$ samples during spin-coating and annealing, as well as after fabrication are displayed in Fig. C.9. The integrated intensities of GIWAXS data corresponding to BNA- and bromide-based compositions with marked phases are displayed in Fig. C.7 (MA-based) and Fig. C.8 (FA-based). For BNA-bromide based compositions, degrees of orientation of $n = 1$ phases and $n = 2$ phases are displayed in Fig. C.9 and Fig. C.10, respectively. A layout of different phases within the final 2D perovskite films with BNA as a spacer cation, iodide or bromide as a halide and MA or FA as a small cation with target dimensionalities of $n = 2$ and $n = 3$ is presented in Fig. C.11.

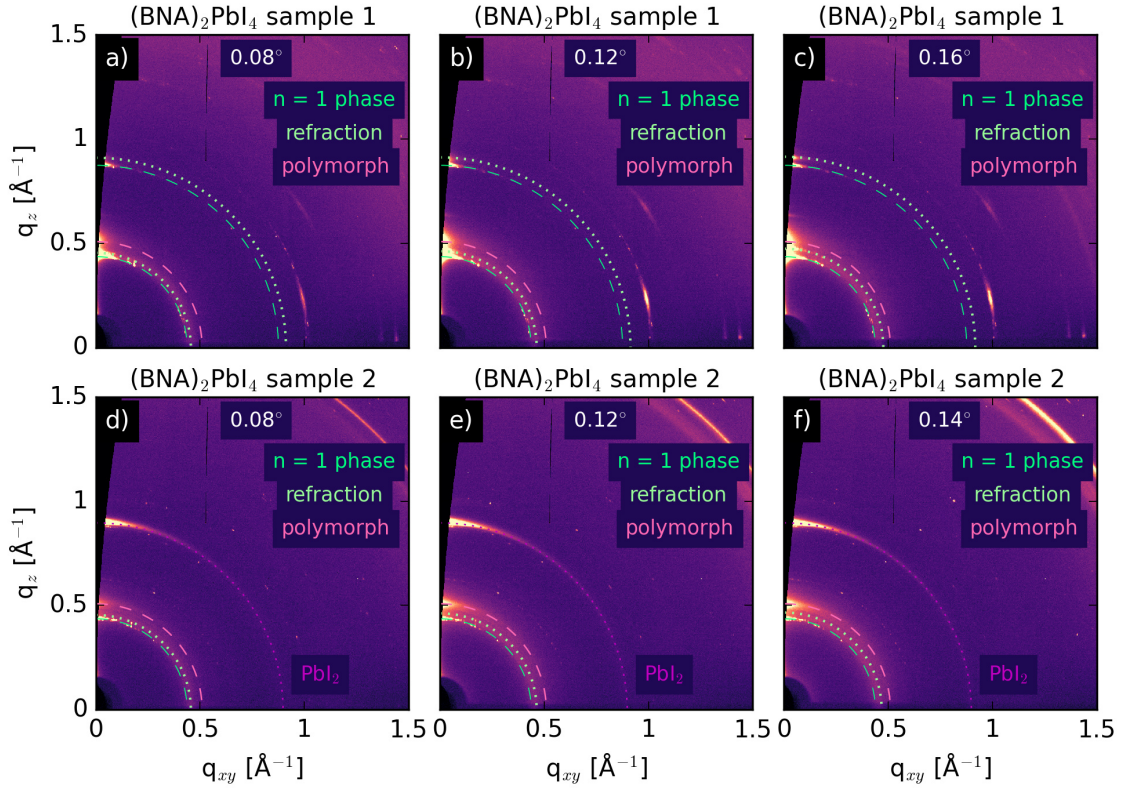


Figure C.1.: GIWAXS data with marked refraction effect^[271] from $n = 1$ phase and $n = 1$ polymorph in (BNA)₂PbI₄ 2D RP composition and other phases. Sample 1 measured at the angle of incidence (a) $\alpha_i = 0.08^\circ$, (b) $\alpha_i = 0.12^\circ$, (c) $\alpha_i = 0.16^\circ$ and sample 2 measured at the angle of incidence (d) $\alpha_i = 0.08^\circ$, (e) $\alpha_i = 0.12^\circ$, (f) $\alpha_i = 0.14^\circ$. Due to the prolonged annealing, sample 2 had some of PbI_2 due to decomposition.

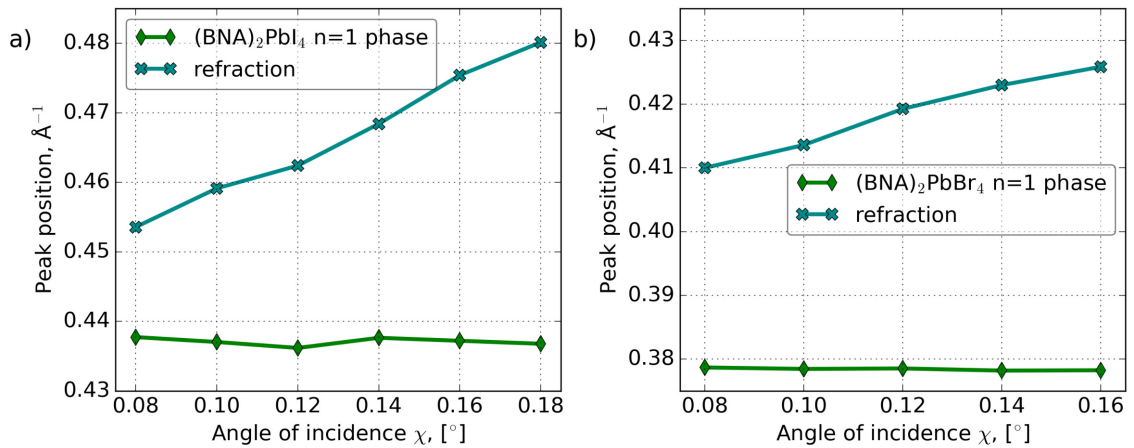


Figure C.2.: Bragg peak positions, showing the refraction effect from $n = 1$ phase in $n = 1$ BNA-based compositions: (a) iodide-based sample; (b) bromide-based sample.

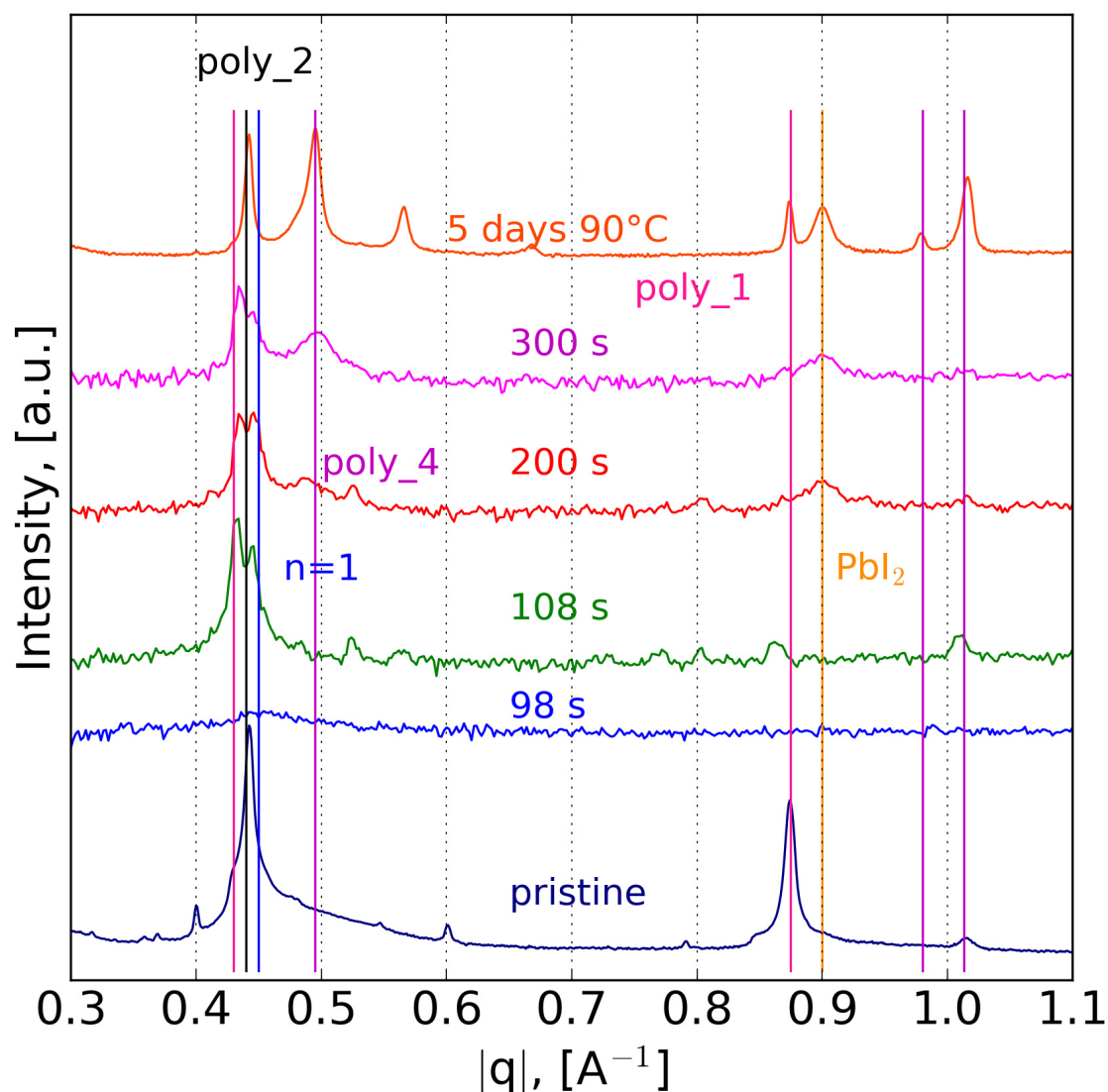


Figure C.3.: Decomposition study of $(\text{BNA})_2\text{PbI}_4$ composition: XRD measured before (pristine) and after annealing at 90°C for 5 days, experiment was done by A. Dučinskas; azimuthally integrated intensities of GIWAXS reciprocal space maps with 0.5° angle of incidence from $(\text{BNA})_2\text{PbI}_4$ sample 1 at the specific moments of the annealing scan: 98 s, 108 s, 200 s, 300 s. The data showed an effect of extensive annealing on thin film structure as well as transformation of the polymorphs during and after annealing, suggesting spacer cation shortage leading to smaller c unit cell parameter. A reflection from poly_2 corresponds to $n = 1$ phase of $(\text{BNA})_2\text{PbI}_4$ [150], while poly_4 is a thermally-degraded polymorph, observed previously as well[178],

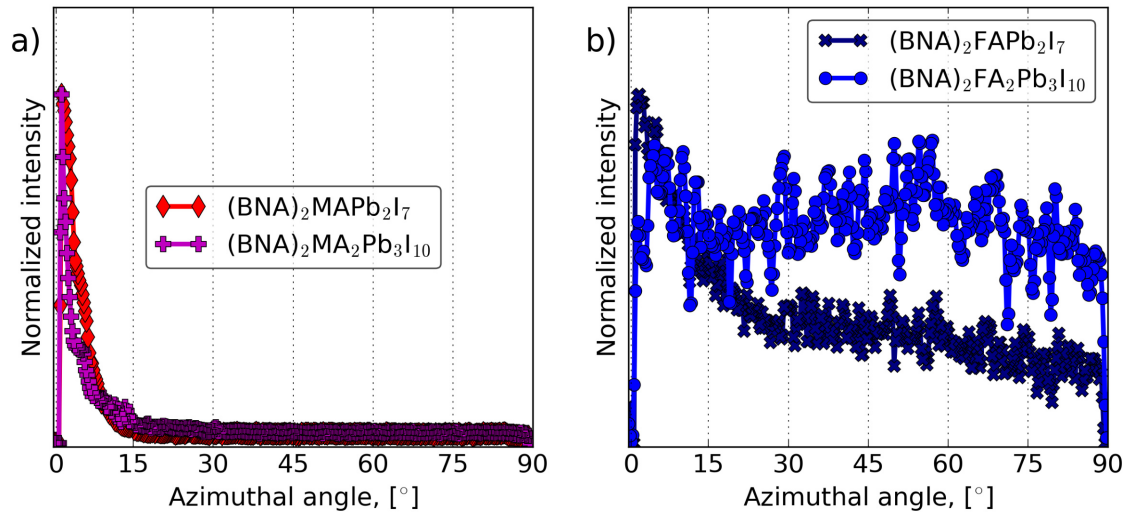


Figure C.4.: Degree of orientation of $n = 1$ phase in BNA-iodide based samples: (a) MA-based and (b) FA-based compositions.

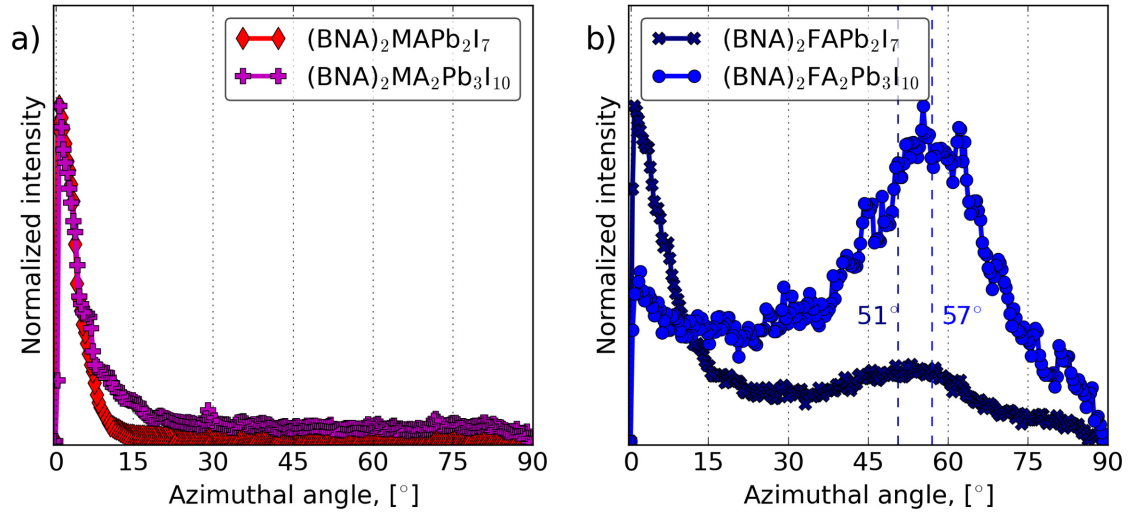


Figure C.5.: Degree of orientation of $n = 2$ phase in BNA-iodide based samples: (a) MA-based and (b) FA-based compositions.

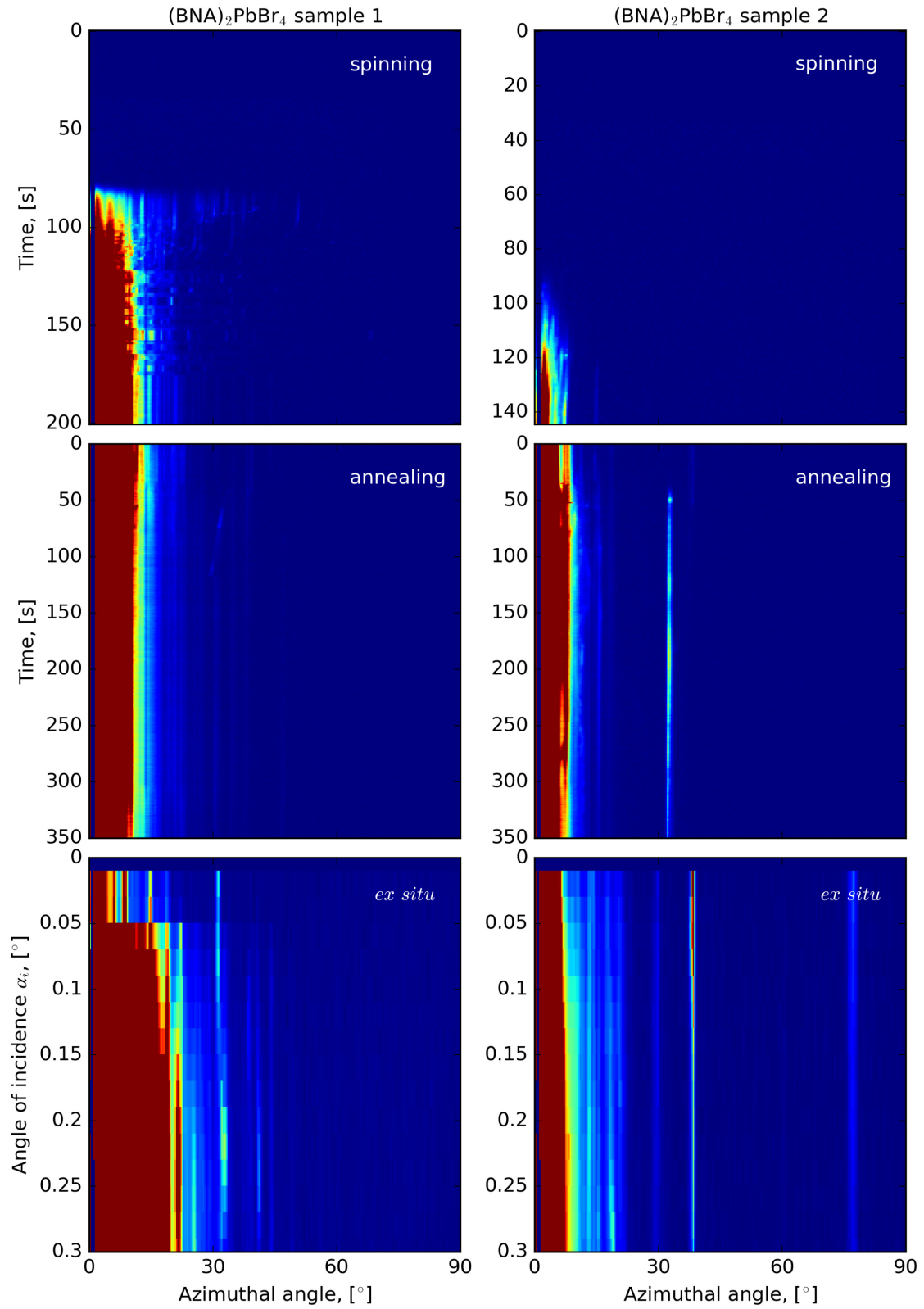


Figure C.6.: Degree of orientation of $n = 1$ phase in $(\text{BNA})_2\text{PbBr}_4$ composition deposited by one step conversion method: sample 1 (left) and sample 2 (right), Top and middle rows represent time evolution during spinning and annealing, respectively, while the bottom row shows the analysis of the *ex situ* measurement of the final film.

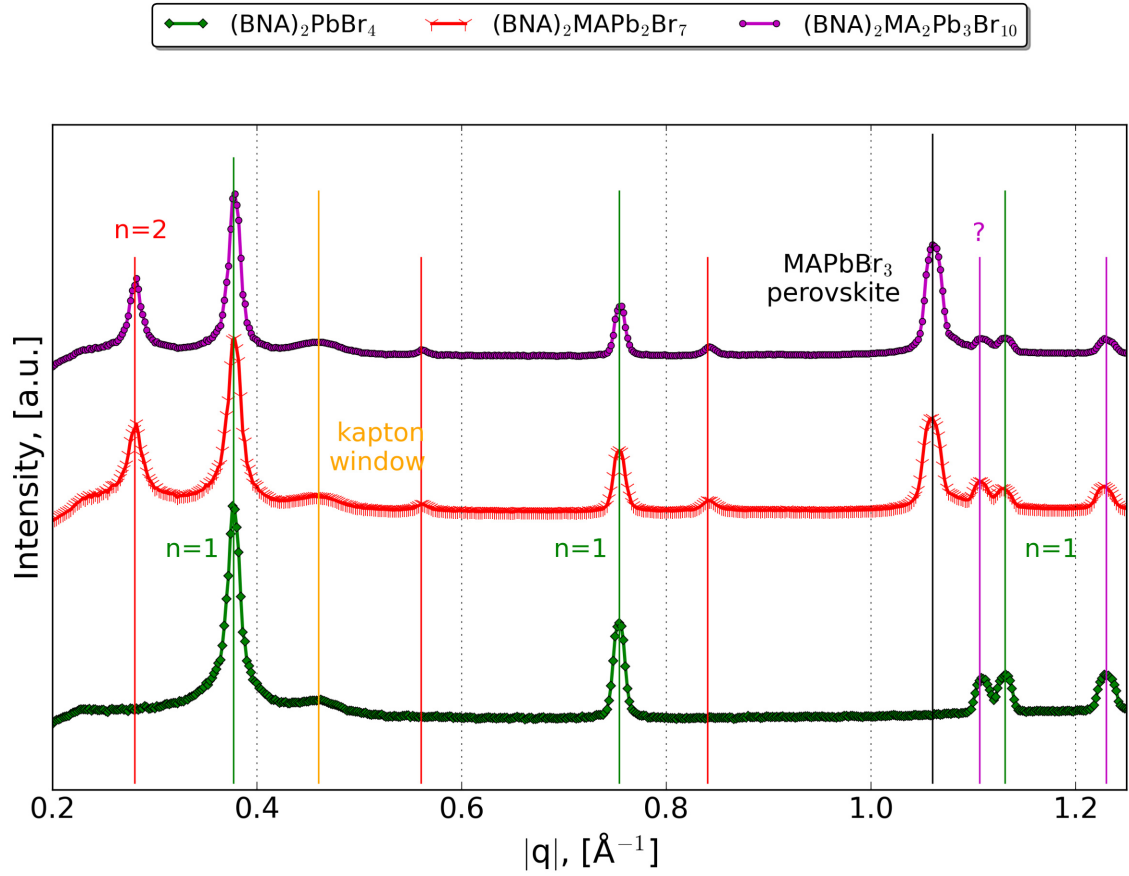


Figure C.7.: Integrated intensity of GIWAXS scans from BNABr $\tilde{n} = 1$ and BNABr-MA $\tilde{n} = 2, 3$ compositions after annealing with marked phases, angle of incidence $\alpha_i = 0.3^\circ$. The question tag

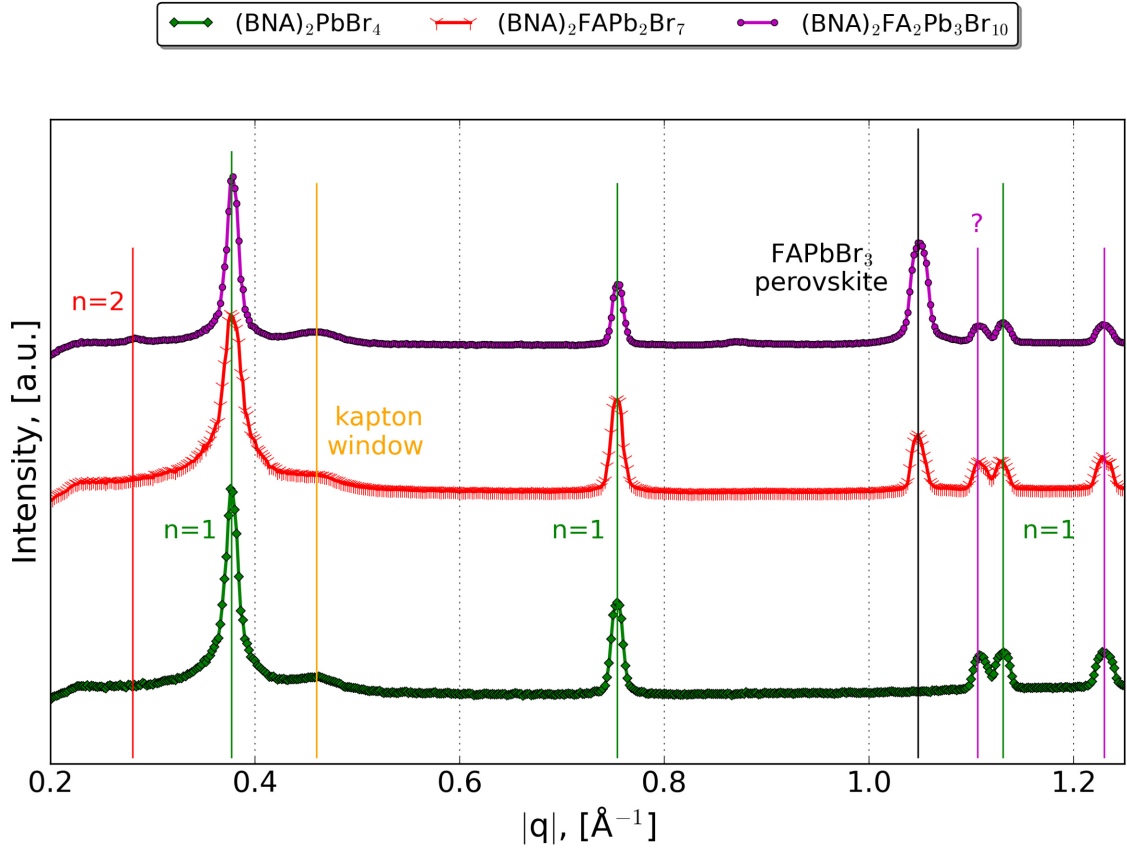


Figure C.8.: Integrated intensity of GIWAXS scans from BNABr $\tilde{n} = 1$ and BNABr-FA $\tilde{n} = 2, 3$ compositions after annealing with marked phases, angle of incidence $\alpha_i = 0.3^\circ$.

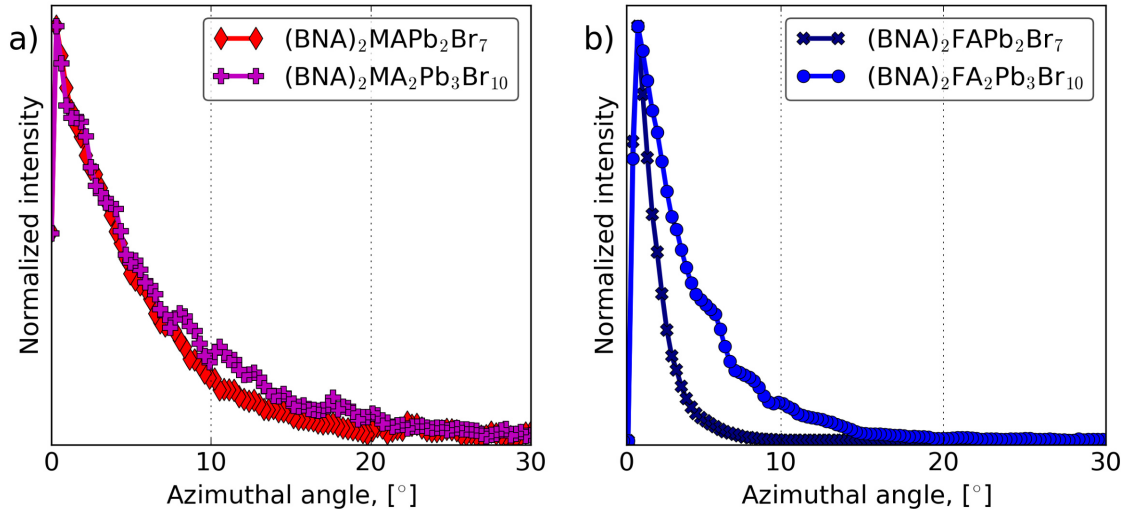


Figure C.9.: Degree of orientation of $n = 1$ phase in BNA-bromide based samples: (a) MA-based and (b) FA-based compositions.

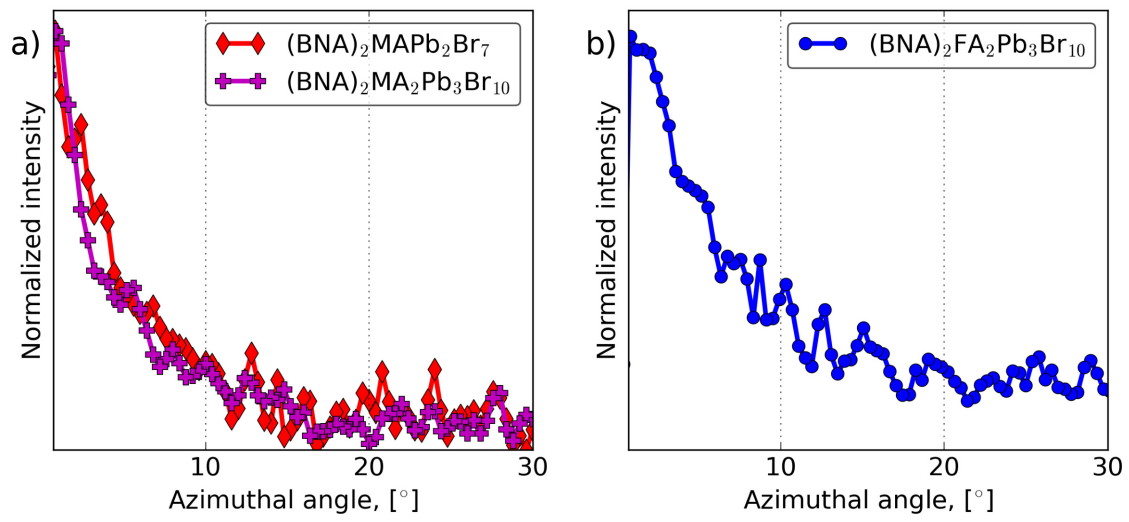


Figure C.10.: Degree of orientation of the $n = 2$ phase in BNA-bromide based samples: (a) MA-based and (b) FA-based compositions;

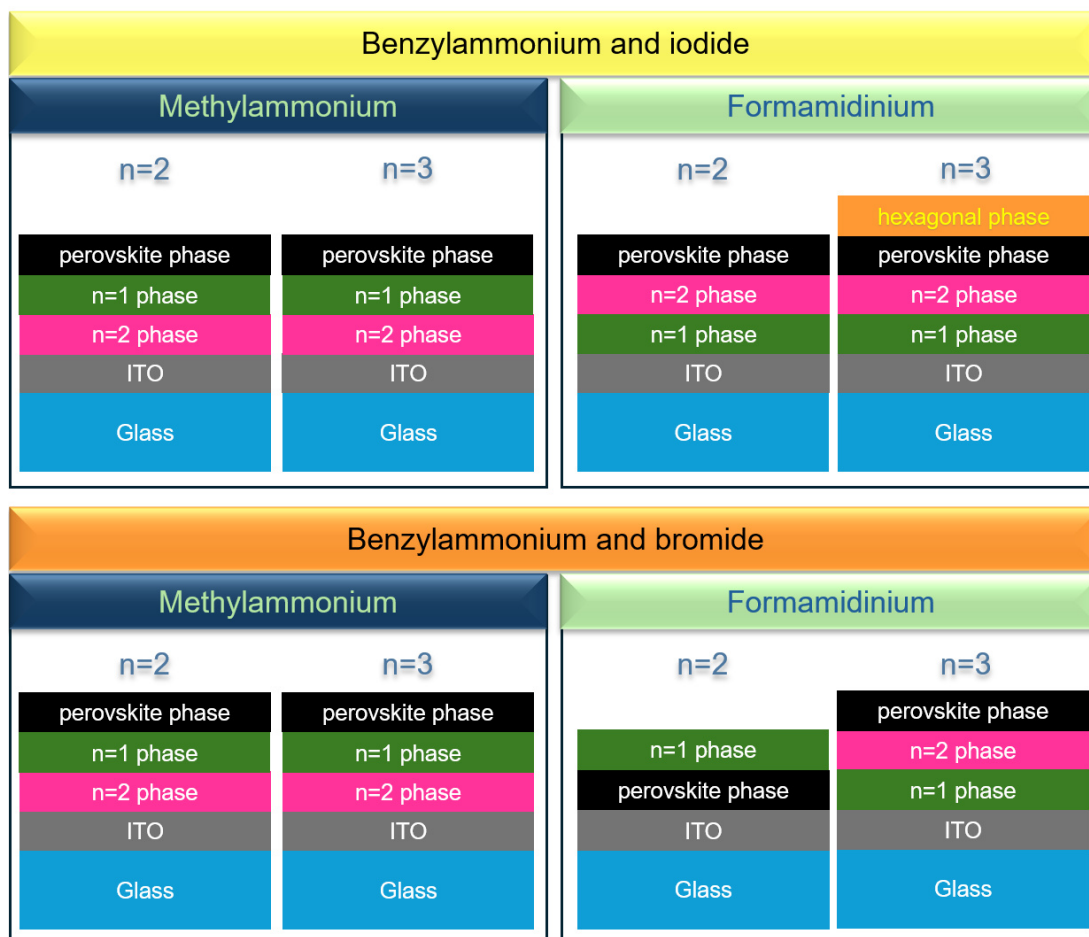


Figure C.11.: Layout of the structures within 2D perovskite samples based on BNA and different halides: iodide (top) and bromide (bottom). The influence of different organic cations, such as methylammonium and formamidinium, and composition dimensionality is displayed. The information on phase composition is extracted from GIWAXS scans from final films, measured at the angle of incidence $\alpha_i = 0.3^\circ$.

D. Datasets used in this work

Tab. D.1 shows all datasets presented in this work, most of them were collected as a result of testing the performance of the designed spin-coating chamber. The additional information on the materials, solutions, substrates, fabrication methods, dates of the beamtimes and in which sections they were discussed can be found within the table.

Table D.1.: A summary of all datasets analyzed in this work for studying crystallization of perovskites and testing spin-coater performance.

Credit for preparing the samples and acquiring the data goes to the respective people. All data analysis presented in this work was performed by E. Kneschaurek. “Data type” announced the main information on the samples, (*) were measured under the kapton dome, while all other samples were grown in spin-coater. “#Samples” refers to the number of samples measured during each beamtime for each method. “Materials” describes the compositions of the deposited thin film. “Solution” announces the solvent or solvent mixture used for perovskite preparation, default mixture is DMF:DMSO (4:1) if not stated otherwise. “Substrate” announces the substrates used for thin film grow. “Year & Month” refers to the date the data was acquired. “Source” refers to the synchrotron source used to conduct the diffraction measurements, i.e. the respective beamline and facility acronym. “Sections” refers to the sections in this work where the results of sample growth evaluation was provided.

Data type	#Samples	Materials & Solutions	Substrate	Month & Year	Source	Sections
3D One step conversion*	7	Tab. 5.2	Tab. 5.2	September 2018	ID10/ESRF	Sec. 5.2
3D DMF intermediate	3	FAPbI ₃ in DMF	Glass/ITO	June 2023	P08/DESY	Sec. 5.4
3D One step conversion	1	FAPbI ₃	Glass	October 2021	P08/DESY	Sec. 5.5
3D One step conversion	4	Tab. 5.5	Glass	December 2021	P08/DESY	Sec. 5.5
3D Antisolvent-assisted	5	Tab. 5.6	Glass	December 2021	P08/DESY	Sec. 5.6
3D Addition of 5% CsI	6	Tab. 5.7	Glass	December 2021	P08/DESY	Sec. 5.7
3D Gas quenching	3	Tab. 5.8	Glass/ITO	March 2022	P08/DESY	Sec. 5.8
2D Benzylammonium iodide	4	$\tilde{n}=1 \times 2$ & MA-based $\tilde{n}=2,3$	Glass/ITO	April 2021	P08/DESY	Sec. 6.2
2D Benzylammonium iodide	2	FA-based $\tilde{n}=2,3$	Glass/ITO	October 2021	P08/DESY	Sec. 6.2
2D Benzylammonium bromide	6	$\tilde{n}=1 \times 2$ & MA-, FA-based $\tilde{n}=2,3$	Glass/ITO	October 2021	P08/DESY	Sec. 6.3
2D DJ	4	Tab. 6.2	Glass/ITO	April 2021	P08/DESY	Sec. 6.4

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List of own publications

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List of acronyms

BMBF Bundesministerium für Bildung und Forschung. 46

BNA Benzylammonium. xiv, xv, 41, 42, 43, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 150, 155, 156, 159, 160, 162, 183, 184, 185, 186, 187, 188, 189, 190, 191

DESY Deutsches Elektronen-Synchrotron. v, vii, x, 46, 47, 48, 49, 60, 68, 69, 88, 165, 166, 193

DFT Density-functional theory. 38, 81, 82, 87, 129, 159

DJ Dion-Jacobson. xv, 40, 41, 43, 131, 148, 149, 150, 152, 153, 154, 155, 156, 160, 162, 193

DMF N,N-dimethylformamide. xiii, 28, 31, 35, 36, 37, 53, 70, 71, 72, 74, 75, 76, 78, 81, 82, 83, 84, 87, 88, 89, 90, 91, 92, 93, 94, 101, 107, 108, 109, 113, 120, 121, 124, 129, 130, 135, 149, 174, 178, 180, 181, 182, 193

DMSO Dimethyl sulfoxide. 28, 30, 31, 35, 36, 53, 72, 74, 75, 76, 78, 81, 82, 83, 84, 85, 87, 90, 93, 95, 96, 101, 103, 105, 108, 109, 110, 111, 112, 113, 114, 115, 116, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 137, 149, 177, 178, 179, 193

DRS Differential reflectance spectroscopy. v, vii, 46, 47, 49, 58, 59, 61, 157, 161, 165, 169, 170

ESC Electronic speed controller. 50, 60, 61

ESRF European Synchrotron Radiation Facility. v, vii, x, 68, 69, 71, 193

FA Formamidinium. xv, 34, 71, 103, 137, 138, 141, 143, 146, 148, 156, 160, 183, 186, 189, 190

FIRA Flash infrared annealing. 168

FTO Fluorine-doped tin oxide. 54, 55, 56, 57, 72, 75, 91, 148, 165, 167

FWHM Full width at half maximum. 18, 19, 20, 76, 77, 79, 97, 118

GIWAXS Grazing incidence wide-angle X-ray scattering. v, vii, xv, 17, 18, 20, 21, 22, 23, 24, 31, 33, 43, 46, 47, 48, 49, 51, 57, 69, 70, 72, 73, 74, 75, 76, 77, 78, 80, 81, 82, 84, 85, 86, 87, 88, 89, 90, 91, 92, 94, 95, 96, 97, 98, 99, 100, 102, 104, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 125, 126, 127, 128, 129, 131, 132, 133, 134, 135, 136, 137, 138, 140, 142, 143, 144, 146, 147, 148, 149, 150, 151, 152, 153, 154, 156, 160, 162, 165, 166, 168, 174, 175, 177, 178, 179, 180, 181, 182, 183, 184, 185, 188, 189, 191

GIXD Grazing incidence X-ray diffraction. 15, 16, 17, 18, 72, 78, 79, 82, 83, 86, 88

GUI Graphical user interface. 60, 62, 68

IPA Isopropanol. xiv, 25, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 114, 115, 116, 117, 118, 119, 120, 121, 122, 124, 126, 127, 130, 132, 158, 159

ITO Indium tin oxide. 25, 54, 55, 56, 57, 88, 89, 92, 96, 120, 132, 135, 136, 138, 141, 149, 162, 168, 183, 193

LED Light-emitting diode. 65

MA Methylammonium. 34, 71, 130, 137, 138, 141, 143, 146, 148, 183, 186, 188, 189, 190

NIR Near-infrared. 54, 55, 56, 60, 61, 62, 68, 89, 99, 167, 168

NIST National Institute of Standards and Technology. 18

OSC One-step conversion. xiv, 69, 70, 71, 80, 88, 89, 90, 91, 93, 98, 100, 105, 108, 109, 111, 112, 113, 114, 119, 121, 123, 124, 126, 129, 130

PDEA 1,4-phenylenediethylammonium. 43, 131, 148, 149, 150, 151, 153, 154, 155, 156, 159, 160, 162

PDMA 1,4-phenylenedimethylammonium. 43, 131, 148, 149, 150, 151, 152, 153, 154, 155, 156, 159, 160, 162

RP Ruddlesden-Popper. 40, 42, 131, 132, 133, 135, 137, 143, 144, 146, 155, 156, 162

SLD Scattering length density. 20, 21

SPI Serial peripheral interface. 66

TRE Total reflection edge. 20, 21

XRD X-ray diffraction. 135, 185

XRR X-ray reflectivity. xv, 18, 20, 135, 137, 138, 141, 148, 149, 150, 151, 156, 162