

X-Ray Investigations on Hybrid Perovskite Thin Films — From Fundamentals to Applications

Dissertation

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Contents

Motivation	ix
Zusammenfassung in Deutscher Sprache	xi
I Background on Perovskites	1
1 Prospects and Opportunities for Perovskite Photovoltaics	3
2 Perovskite and Related Structural Phases	7
2.1 The (Ideal) Cubic Perovskite Structure	8
2.2 Distorted Perovskite Structures	10
2.3 Layered Perovskitoid Phases	12
2.4 Non-Perovskite Phases	15
2.5 Solvent Complex Intermediates	18
3 Composition Dependent Properties of Perovskite Materials	23
3.1 General Properties	23
3.2 Changing the Central Cation	27
3.3 Influence of the Halide	31
3.4 Layered Perovskite Materials	33
4 Thin Film Growth and Device Fabrication	37
4.1 Perovskite Thin Film Growth	37
4.2 Crystallization of Perovskite Phase	39
4.3 Device Fabrication	43
5 Challenges	45
5.1 Environmental Impact	45
5.2 Upscaling	50

5.3	Stability	51
II	Experimental Methods	53
6	X-Rays and Their Interaction with Matter	55
6.1	Refraction and Reflection	57
6.2	Absorption and Scattering	59
6.3	X-Ray Diffraction	60
7	X-ray Techniques	63
7.1	Grazing Incidence Wide Angle X-Ray Scattering	63
7.2	X-Ray Reflectometry	68
7.3	X-Ray Sources and Experimental Setup	70
7.4	Resonant ‘Anomalous’ Scattering and Diffraction	73
8	Perovskite Thin Film Fabrication	85
8.1	Spin-Coating	85
8.2	Solvent Engineering — Antisolvent Quenching	87
8.3	Gas Quenching	89
8.4	Vapor Deposition	90
III	Results and Discussion	91
9	Effects of Component Mixing on the Structure, Properties and Growth of Perovskite Thin Films	93
9.1	Quantifying Stabilized Phase Purity in Formamidinium-Based Multiple-Cation Hybrid Perovskites	94
9.2	Host-Guest Complexation of Cesium Cations for Fabrication of Gradient Structures	104
9.3	Increase of Non-Perovskite FAPbI ₃ Phase by Imidazolium Inclusion	111
9.4	Halide Segregated Crystallization of Mixed Halide Perovskites	114
9.5	Final Remarks on Mixed Perovskite Compositions	127
10	Modifying Perovskite Thin Film Growth and Grain Morphology by Additives — The Example of Thiourea	129
10.1	Effects of Thiourea Addition on MAPbI ₃ Thin Film Growth During the Full Fabrication Route	130

10.2	Influence of Crystallization Kinetics on the Effects of Thiourea	140
10.3	Compositional Dependence of the Effect of Thiourea	148
10.4	Final Remarks on the Effects of the Thiourea Additive	157
11	Structural Properties of Layered Perovskites Dictated by Spacer Cations and Perovskite Compositions	159
11.1	Structural Complexity of Formamidinium-Based Dion-Jacobson Layered Hybrid Perovskites with the PDMA ²⁺ Spacer Cation	161
11.2	Further Parameters Influencing PDMA-based Layered Structures — Substrate, Halide Anion and Solvent	168
11.3	The Role of Alkyl Chain Length and Halide Counter Ion in Layered Dion-Jacobson Perovskite Phases With Aromatic Spacers	174
11.4	BNA ⁺ and PEA ⁺ for Ruddlesden-Popper Phases and Perovskite Phase Stabilization	181
11.5	Supramolecular π -Templating in Ruddlesden-Popper Phases with Mixed Spacer Cations	191
11.6	Final Remarks on the Structural Properties of Layered Perovskites	199
12	Advanced Preparation Methods For Perovskite Thin Films	203
12.1	Preserving the Stoichiometry of Triple-Cation Perovskites by Carrier-Gas-Free Antisolvent Spraying	204
12.2	Enhancing Luminescence Efficiency by Controlled Island Formation of CsPbBr ₃ Perovskite	207
12.3	Final Remarks on Advanced Preparation Methods	210
13	Devices: Perovskite-Organic Tandem Solar Cells with Indium Oxide Interconnect	211
IV	Summary and Outlook	221
V	References	227
	Appendices	263
A	List of Own Publications	265

B	Abbreviations	271
C	Experimental Details	275
C.1	General Fabrication and Measurement Details for All Samples	275
C.2	Experimental Details for Fabrication of CsPbBr ₃ and CsSnBr ₃ Thin Films in Section 7.4	278
C.3	Experimental Details for Fabrication of Thin Films with Thiourea Additive in Chapter 10	279
D	Additional Data	281
E	Acknowledgements	321

Motivation

Since the discovery of their photovoltaic capabilities,¹ hybrid metal organic halide perovskites have made a stellar rise in the field of photovoltaics. Continuing to set new record efficiencies, as of now, lab scale perovskite solar cells have reached comparable power conversion efficiencies as state-of-the-art silicon-based solar cells.² This renders perovskite cells an exciting competitor, which might offer the possibility to be fabricated in more cost efficient and less energy demanding processes.^{3,4} The main appeal of perovskite solar cells, however, does not lie in replacing established photovoltaic materials, but in their complementation, either in joint applications like tandem cells, or in offering new implementation opportunities. These might include curved or flexible substrates,^{5,6} semitransparent^{7,8} or even switchable solar cells.^{9,10} Apart from photovoltaics, hybrid perovskite materials offer a large variety of other potential technical employments, such as radiation detectors,¹¹ light emitting diodes^{12–16} or even lasers.¹⁷

For all these applications, a fine tuning of material properties is vital. These can be heavily altered by even minor scale variations in material composition, morphology and microscopic structure. Since the latter two depend strongly on the fabrication process and its parameters,^{18–22} these require careful optimization. Therefore, structural investigation of hybrid perovskite materials provides key data for determining the correlation of structure, properties and the material fabrication. Despite the final materials holding important structural information as well, in-situ measurements during the crystallization and preceding processes are key to understanding the full influences of all parameters.^{23,24} For this purpose, X-ray diffraction experiments are an apposite tool since they offer non-invasive investigation. Combined with synchrotron radiation, this provides a subsecond temporal resolution that is well suited for observing the time scales of (pre-)crystallization processes.

This thesis summarizes various studies on the investigation of hybrid metal organic halide perovskite materials applying X-ray techniques. The selection of studies showcases the variability of both the perovskite materials and X-ray based techniques, providing an overview of the wide range of possibilities which both of these fields offer.

Zusammenfassung in Deutscher Sprache

Seit der Entdeckung ihrer photovoltaischen Fähigkeiten haben hybride metallorganische Halogenid-Perowskite einen steilen Aufstieg auf dem Gebiet der Photovoltaik erlebt. Perowskit-Solarzellen im Labormaßstab erreichen mittlerweile vergleichbare Wirkungsgrade zu modernen Solarzellen auf Siliziumbasis. Dies macht Perowskit-Solarzellen vielversprechend konkurrenzfähig, da sie potentiell kosteneffizienter und in weniger energieaufwendigen Verfahren hergestellt werden können. Das eigentliche Potential von Perowskit-Solarzellen liegt jedoch nicht im Ersatz etablierter Solarzellenmaterialien, sondern in deren Ergänzung. Dies beinhaltet kombinierte Anwendungen wie Tandemzellen, aber auch die Ermöglichung neuer Verwendungsbereiche. Neben Photovoltaik bieten hybride Perowskit-Materialien eine Vielzahl weiterer technischer Einsatzmöglichkeiten, wie beispielsweise Röntgendetektoren, Leuchtdioden oder Laser.

Für all diese Nutzungsweisen ist eine exakte Anpassung der Materialeigenschaften unerlässlich. Diese können jedoch schon durch geringfügige Abweichungen in der Materialzusammensetzung, der Morphologie und der mikroskopischen Struktur stark beeinflusst werden. Da die beiden letztgenannten Eigenschaften zu großen Teilen vom Herstellungsprozess und seinen Parametern abhängen, ist eine Optimierung dieser maßgebend. Die Analyse von Kristallstruktur und Morphologie hybrider Perowskit-Dünnschichten liefert daher wesentliche Anhaltspunkte für die Bestimmung des Zusammenhangs zwischen Struktur, Eigenschaften und Herstellung dieser Materialien.

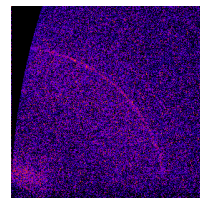
Obwohl auch die fertigen Perowskit-Schichten wichtige strukturelle Informationen enthalten, sind in-situ-Messungen während der Dünnschicht-Abscheidung, der Kristallisation und vorhergehender Prozesse der Schlüssel zum Verständnis der vollständigen Einflüsse aller Parameter. Zu diesem Zweck sind Röntgenbeugungsexperimente ein geeignetes Instrument, da sie nicht-invasive Untersuchungen ermöglichen. Die Kombination mit Synchrotronstrahlung bietet eine zeitliche Auflösung im Subsekunden-Bereich, die die Beobachtung von (Prä-)Kristallisationsprozessen ermöglicht.

Diese Arbeit fasst verschiedene Studien zur Untersuchung von hybriden metallorganischen Halogenid-Perowskit-Materialien mittels Röntgen-Analysetechniken zusammen. Die Aus-

wahl der Studien zeigt die Variabilität sowohl der Perowskit-Materialien als auch der röntgenbasierten Analyse und bietet einen Überblick über die vielfältigen Möglichkeiten, die die Kombination dieser beiden Bereiche bietet.

So werden neue Erkenntnisse über die Auswirkungen der Mischung von Materialkomponenten auf die Kristallstruktur und die Dünnschichtmorphologie sowie über die Effekte und Wirkungsmechanismen von Prozess-Additiven erlangt. Darüber hinaus wird eine umfassende Strukturanalyse von perowskitähnlichen Schichtstrukturen mit molekularen Abstandshaltern gegeben. Schließlich werden Röntgenanalysen komplexer Herstellungsmethoden für Perowskit-Heterostrukturen sowie funktionstüchtiger Solarzellen präsentiert, die die technische Relevanz der vorliegenden Arbeiten demonstrieren.

I BACKGROUND ON PEROVSKITES



Chapter 1

Prospects and Opportunities for Perovskite Photovoltaics

This brief introductory chapter maps out the opportunities of hybrid perovskite materials and their possible technological employment to underline the relevance of research on these materials. The subsequent chapters expand on the scientific foundations in detail. Materials exhibiting the perovskite structure have been known for a long period of time and are utilized in various applications like superconduction or catalysis.²⁵ The group of Miyasaka was the first to investigate a hybrid metal organic halide perovskite material as a photoactive component in a dye-sensitized solar cell.¹ Although this first study in the year of 2009 showed only a small power conversion efficiency of 3.8 %, since then intense research efforts led to an increase in efficiency towards values close to commercial silicon-based solar modules within not even 15 years, as depicted in Figure 1.1.² Therefore, perovskite solar cells not only offer the possibility of cost-efficient and energy-reduced production, but additionally comprise the potential to provide higher efficiencies than current technologies, especially in tandem applications, exploiting the already existing techniques complemented with perovskite solar cells.^{2, 26–28}

The solution based fabrication processes, with which these perovskite materials can be produced, take low effort to implement, are scalable and require no high-energy processing steps as for example in silicon crystallization. Even though wet-chemical methods generally lead to defect-rich materials, the semiconducting and photovoltaic properties of the fabricated perovskites have shown to be promising.⁴ Defect tolerance is one of the unique properties of hybrid perovskite materials, making them a favorable material class for solution-based production of devices.^{29–32}

The high solar cell efficiency of perovskites can be ascribed to a combination of sev-

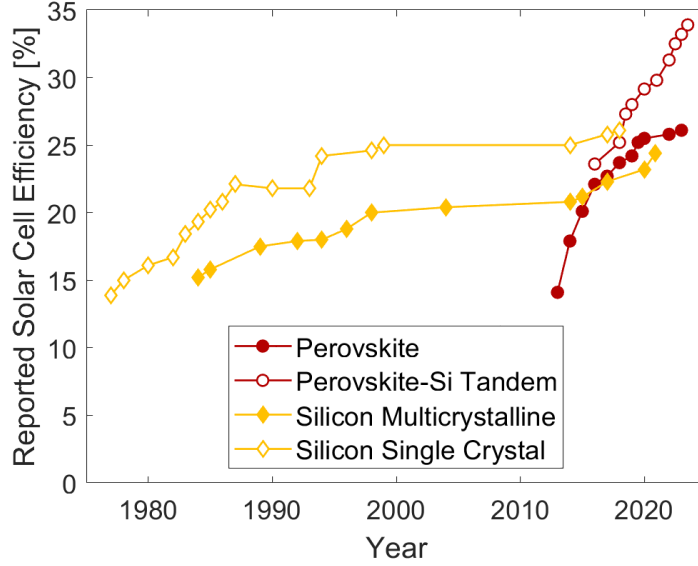
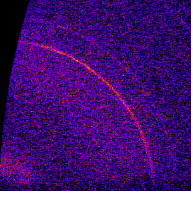
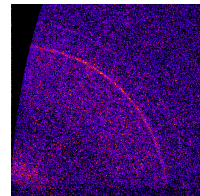


Figure 1.1: Reported solar cell efficiencies for selected technologies, showing perovskite solar cells increasing rapidly to surpass common photovoltaic technologies such as silicon solar cells. Data taken from [2].

eral unique properties enabling efficient conversion of sunlight into electricity. Perovskite materials possess a high optical absorption coefficient over a large wavelength range, including not only visible light, but parts of the near-infrared spectrum as well.^{4,33} This enables the application of relatively thin layers of material, down to several hundreds of nanometers in thickness.³⁴ The electronic properties and thus the band gap and range of absorption, however, are tunable by altering the material composition. This allows the creation of perovskite solar cells that are optimized for different types of applications, including single-junction and tandem solar cells. Ranges of 1.25–2.23 eV^{35–37} have shown to be feasible for the band gaps of commonly applied hybrid perovskite materials, where the band gap is direct and thus leads to a strong, abrupt absorption onset.³⁵ Furthermore, the perovskite band structure itself is optimal for charge carrier extraction, due to the strongly dispersive conduction and valence bands, leading to a small effective mass of charge carriers.^{29,38–40} Together with the long charge carrier diffusion length of these materials, this is a prerequisite for efficient charge separation.^{41,42}

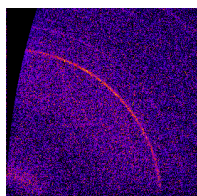
Since ionic migration is considered to be an intrinsic property of hybrid metal halide perovskites,⁴³ this can lead to a facile decomposition pathway, but opens the possibility for self-healing as well.⁴⁴ In general, hybrid perovskites are far softer materials than inorganic semiconductors, but stiffer than conventional soft materials like organics due to

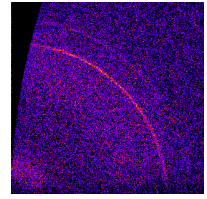


CHAPTER 1. PROSPECTS

the wide range of interactions between the constituents, reaching from van-der-Waals and hydrogen bond interactions up to bonds of ionic and covalent character.⁴⁵ The presence of organic cations and their rotational degrees of freedom induce a novel structural parameter, which leads to unique material properties, such as high polarizability, the possibility for dipole alignment including ferroelectric behavior^{44, 46} and piezoelectricity.^{47, 48} These unique properties render hybrid perovskite materials highly suitable for several further applications, including light emitting diodes (LEDs),^{12–16, 49, 50} lasing^{17, 51} and radiation detection.¹¹

In the following sections, the perovskite and its related structures are portrayed first in Chapter 2, then the material specific properties of the most important perovskite formulations, depending on the material composition, are described in Chapter 3. Details of the thin film growth process, perovskite crystallization and the device fabrication are featured in Chapter 4. Challenges and obstacles, which need to be overcome for successful device production are presented in Chapter 5.





Chapter 2

Perovskite and Related Structural Phases

This chapter introduces the perovskite structure and its derivatives as well as possible non-perovskite structures which frequently occur during perovskite thin film fabrication processes, including intermediate solvent complexes.

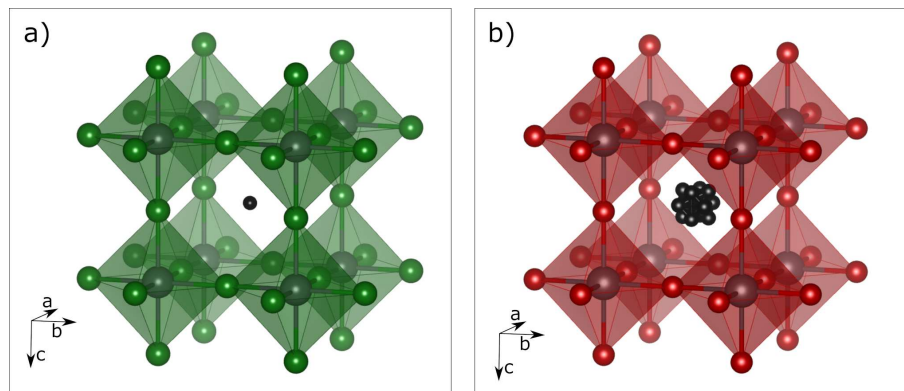
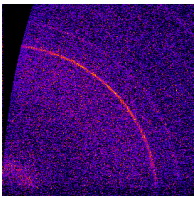


Figure 2.1: Cubic perovskite crystal structures of (a) MAPbI_3 ⁵² and (b) MAPbBr_3 .⁵³ Green spheres: iodide, red spheres: bromide, large gray spheres: lead, small black spheres represent methylammonium. The single black sphere in (a) indicates the ideal position of the methylammonium (MA^+) cation. The many black spheres in (b) represent different orientations of the methylammonium cation. Note that for both iodide and bromide-based compositions, methylammonium adopts several possible orientations as shown in (b).



2.1 The (Ideal) Cubic Perovskite Structure

The perovskite structure was first discovered in the mineral of calcium titanate (CaTiO_3),⁵⁴ which was named perovskite after the mineralogist Lev Perovski, and serves nowadays as a namesake for a whole structural class of materials. Common to all perovskite materials is a composition including three different types of ions which occupy three distinct positions within the unit cell, generally represented as ABX_3 composition. The ideal cubic perovskite structure is depicted in Figure 2.1. In the materials discussed in this work, A stands for the central univalent cation, which in most cases is a small organic molecular cation, such as methylammonium (MA^+) or formamidinium (FA^+), both of which are shown in Figure 2.2. In some cases this is also an inorganic cation such as cesium. B indicates the bivalent metal cation, which generally is lead. Less frequently, tin is applied as well. Finally, X represents the halide anions, which are usually iodide, bromide or mixtures thereof. Commonly, in the realm of hybrid organic-inorganic metal halide perovskites, for each of these positions likewise a mixture of the mentioned ions, including more, can be, and often is, utilized.

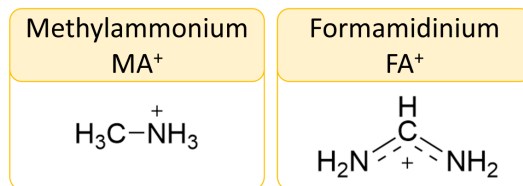
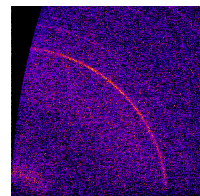


Figure 2.2: Molecular formulae of methylammonium (MA^+ , IUPAC name: methanaminium) and formamidinium (FA^+ , IUPAC name: aminomethylideneazanium), the two most widely employed organic cations in hybrid perovskite compositions.

Characteristic for the perovskite structure is a network of corner-sharing BX_6 octahedra, where the space between them contains the larger cation. In general, a perovskite structure can be formed by any three kinds of ions which respect the constraints of charge neutrality when mixed in an ABX_3 ratio and of the ionic radius to fit the structure. For the latter, Goldschmidt's tolerance factor⁵⁵ t is applied as a measure of how well the chosen ions are suited to form a cubic perovskite structure. It is calculated via

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \quad (2.1)$$

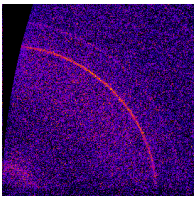
Here, R_A , R_B and R_X are the ionic radii of the respective ions. For the tolerance factor t , values between 0.8 and 1.0 are considered the best fit for forming a cubic perovskite



CHAPTER 2. STRUCTURES

structure. For values below or above, there is the possibility of forming a distorted perovskite structure, as described in the next section, or non-perovskite structures are formed, which are discussed in Section 2.4.

Although the high symmetry, high temperature perovskite phase is often described as possessing a cubic symmetry, the structures are likely not centrosymmetric.^{46, 48, 56} A certain disorder of the organic cations and the halides is observed in the cubic phase as well, in such a way that the organic cation can occupy different orientations with equal probability as visualized in Figure 2.1 (b).^{53, 57} Halide disorder is reflected in disordered PbX_6 octahedra,⁵⁷ often leading to the structures being pseudo-cubic.³⁵ This facilitates distortion into non-cubic structures, which is described in the next section.



2.2 Distorted Perovskite Structures

Most perovskite materials can adopt several differing structural phases, depending on e. g. temperature and pressure, influenced by the material composition.^{35,57–68} The highest symmetry cubic (or often pseudo-cubic) phase is adopted at relatively high temperatures, depending on the material composition. Decreasing the temperature below the material-specific phase transition temperature will lead to a phase transition involving symmetry reduction. However, the general motif of corner-sharing lead halide (or, more general, BX_6) octahedra is retained. Rotation, tilt and deformation of those can lead to the aforementioned symmetry reduction and deformation of the unit cell into other crystal symmetries such as tetragonal or orthorhombic structures, depending on the material composition.³⁵ Usually the highest symmetry cubic phase is referred to as α -phase, while with subsequent symmetry (and temperature) reduction, the resulting phases are called β and γ -phase.⁶⁸ Those can still be photoactive perovskite phases. As a general trend, β and γ -phases tend to show tetragonal and orthorhombic symmetry,^{35,62} respectively. However, not all material compositions necessarily adopt all phases.³⁵

Tetragonal Phases Tetragonal phases are derived from the ideal cubic perovskite phase by tilting of the lead halide octahedra.³⁵ This reduces the crystal symmetry and can lead to multiple twinning with the crystal adopting several different domains.⁶⁹ Tilting of the octahedra can occur out-of-phase, as for example for methylammonium-based compounds, or in-phase as for compounds containing formamidinium or cesium cations.³⁵ A possible

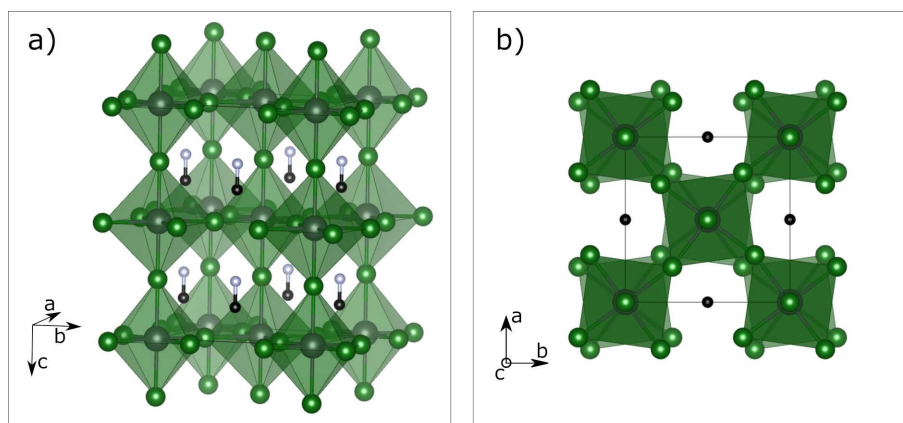
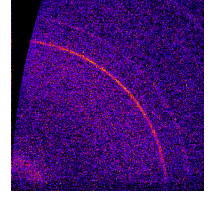


Figure 2.3: Crystal structure of the tetragonal MAPbI_3 β -phase.³⁵ Green spheres: iodide, large gray spheres: lead, black spheres: carbon, light slate blue spheres: nitrogen. View along the c -axis in (b) showcases octahedral tilting. Hydrogen atoms are omitted.



resulting structure, in this case for MAPbI_3 , is shown in Figure 2.3. The tetragonal phase can be distinguished from the cubic perovskite phase in X-ray diffraction patterns by a characteristic splitting of peaks as well as by the appearance of distinct new peaks. Optoelectronic properties have shown to be rather similar for the cubic and tetragonal structures of MAPbI_3 ,⁷⁰ which only differ by small variations in the local structure and are assumed to coexist in the same material.⁶³ Since the rotation angle increases monotonically upon transition from the cubic to the tetragonal structure, it can serve as an order parameter for the transition.⁷¹

Orthorhombic Phases Upon further decrease of the temperature, most perovskite materials undergo a further symmetry reduction from the tetragonal into an orthorhombic structure and a low symmetry super-lattice is formed.³⁵ This symmetry reduction, similar to the transition from the cubic to the tetragonal phase features a characteristic rotational tilt of the lead iodide octahedra, which increases compared to the tetragonal phase and includes a second rotation axis. An example for a low-temperature orthorhombic perovskite structure is shown in Figure 2.4, where the two different directions of view visualize the octahedral tilt.

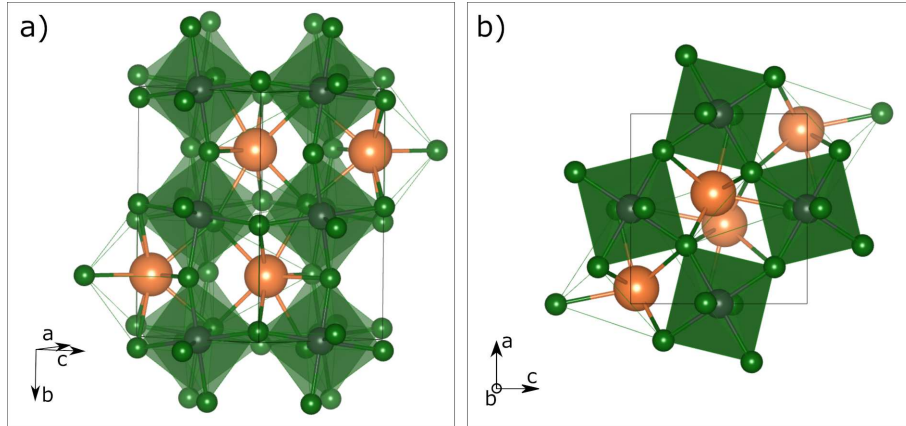
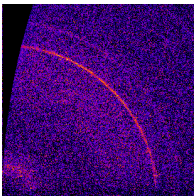


Figure 2.4: Crystal structure of the orthorhombic CsPbI_3 γ -phase.⁷² Green spheres: iodide, large gray spheres: lead, largest orange spheres: cesium. The view along different directions in (a) and (b) showcases octahedral tilting around two rotational axes.



2.3 Layered Perovskitoid Phases

Layered perovskitoid, for simplicity also termed as perovskite, phases are phases with a similar structural motif of corner-sharing BX_6 octahedra. However, instead of a three-dimensional network of octahedra, they feature two-dimensional slabs of these, which are separated by layers of molecular cations.^{45,73–75} Hence, they are commonly called 2D-perovskites. Quasi-2D perovskites contain thicker inorganic slabs, consisting of several layers of lead halide octahedra. The number of inorganic layers within one slab is commonly represented by the number n , as indicated in Figure 2.5. These materials require a mixture of small and larger molecular cations for the layered higher n phases to form. The molecular cations for layered phases, often termed as ‘spacer molecules’, usually possess a quite anisotropic shape, in such a way that they are elongated in one spatial direction, making them rod-shaped, or they can even contain aromatic rings or additional functional groups. Examples of molecular cations commonly applied in layered perovskite phases are presented in Section 3.4. Due to the discontinuity of the lead halide network in the direction perpendicular to the layers, the stoichiometry of the material is altered to A'_kPbI_4 , with k being either 1 or 2 depending on the number of functional groups of the large molecular cation A' , creating a double or single layer of spacers between the perovskite slab as described below to form Ruddlesden-Popper or Dion-Jacobson phases. For the quasi-2D perovskite materials, this leads to a general formula of $A'_kA_{n-1}Pb_nI_{3n+1}$, where A is the small cation forming the 3D-like parts of the network and n is the number

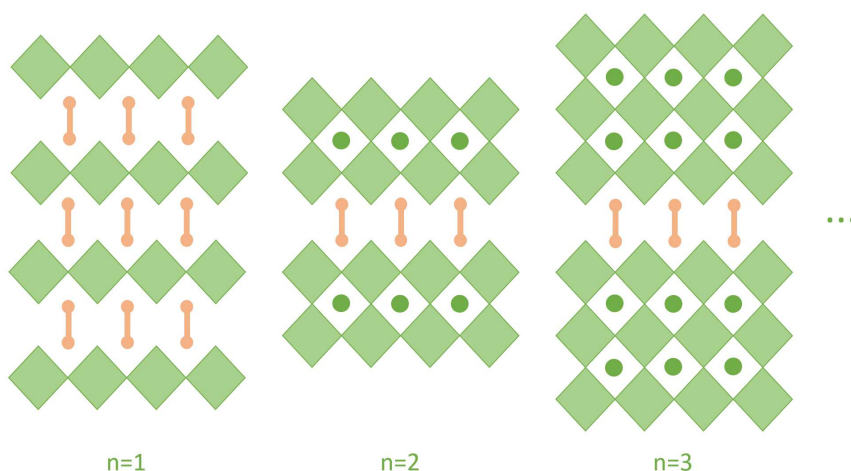


Figure 2.5: Schematic representation of layered 2D perovskite structures with different number of lead halide layers n . Green squares: projected representation of lead halide octahedra, green circles: small central cation, orange dumbbells: spacer cations.

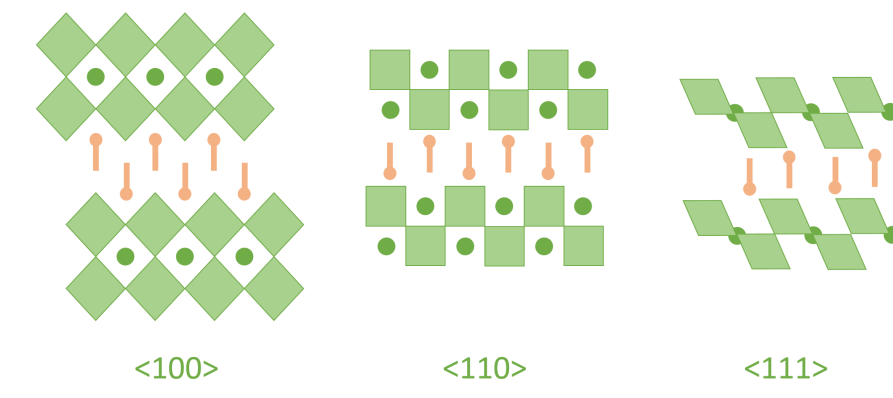
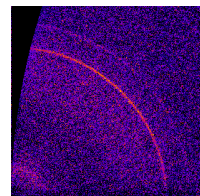


Figure 2.6: Schematic depiction of layered 2D perovskite structures with different split directions through the 3D perovskite network. Green squares: projected representation of lead halide octahedra, green circles: small central cation, orange shapes: spacer cation.

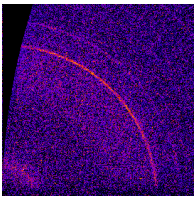
of perovskite layers between adjacent organic spacer layers.

Additional to the number of layers of lead halide octahedra and the valence of the spacer cation, a further classification parameter for (quasi-)2D perovskite structures is the ‘split direction’ of the lead halide network to obtain the 2D slabs, which can be along the (100), (110) or (111) crystallographic direction. Examples for the different structures are shown in Figure 2.6. The most common split direction is along (100), while the others are observed in rarer cases, employing special structure-directing molecular cations.^{45,74}

Ruddlesden-Popper Phases Ruddlesden-Popper (RP) phases are characterized by a double layer of molecular cations between the inorganic slabs.^{78–81} Therefore, monovalent spacer cations are required to form these phases, leading to a stoichiometry of $A'_2A_{n-1}M_nX_{3n+1}$.

The lead halide layers in RP phases usually are stacked with an offset per unit cell, most often of about half the cell parameter.⁷⁸ A double layer of spacer cations can lead to a relatively large distance between the lead halide slabs, which creates well-isolated layers with barely any interactions between them. An example for a Ruddlesden-Popper structure is depicted in Figure 2.7 (a).

Dion-Jacobson Phases In Dion-Jacobson (DJ) phases, the inorganic slabs are separated by a single layer of molecular cations.^{82–84} Hence, those are bivalent, with a singly charged functional group at either end of the spacer to interact with the inorganic slabs, leading to an $A'A_{n-1}M_nX_{3n+1}$ stoichiometry. Consequently, the layers are commonly



2.3. LAYERED PEROVSKITOID PHASES

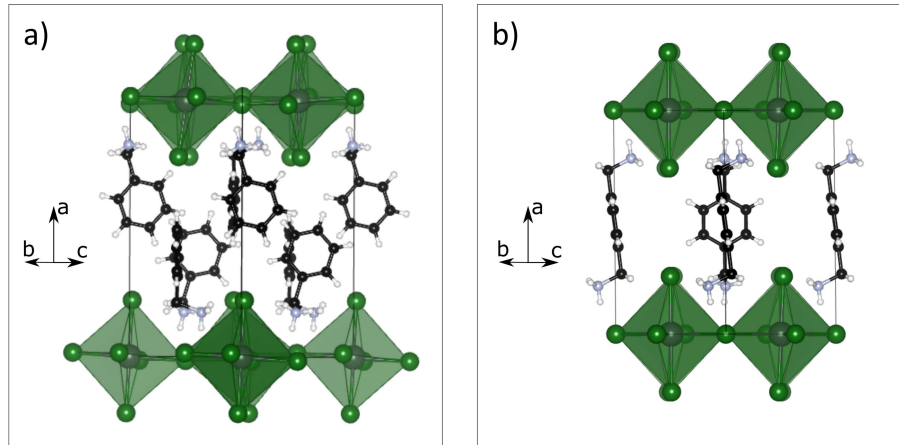
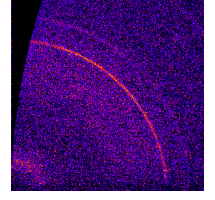


Figure 2.7: Examples for layered 2D perovskite crystal structures. (a) Ruddlesden-Popper phase⁷⁶ (b) Dion-Jacobson phase.⁷⁷ Green spheres: iodide, large gray spheres: lead, small black spheres: carbon, small slate blue spheres: nitrogen, smallest white spheres: hydrogen.

closer than in RP phases containing molecular ions of similar size and shape. In addition, the inorganic slabs are stacked directly on top of each other⁸⁵ with increased interlayer-interactions as compared to the RP phases.⁷³ Figure 2.7 (b) shows an example for a Dion-Jacobson structure.



2.4 Non-Perovskite Phases

Most materials, which possess the appropriate composition to form a perovskite structure, can also form non-perovskite structures instead. For certain material compositions, they are even favored over the perovskite-type.^{86,87} In contrast to the perovskite structures, the three dimensional network of corner-sharing BX_6 octahedra is not retained. Instead, edge and face-sharing structures are commonly found, or combinations of different connectivities. This is mostly disadvantageous for the optoelectronic properties since the band gap increases with a reduced amount of corner-sharing octahedra.⁸⁸ Generally, the non-perovskite phase is referred to as δ -phase. The δ -phase can, however, exhibit different crystal symmetries depending on the material composition. Here, a selection of the non-perovskite structures that appear most frequently in hybrid metal halide perovskite formulations are described.

Linearly Arranged Hexagonal Phase Some materials, above all FAPbI_3 , tend to form hexagonal structures, where the BX_6 octahedra exhibit a face-sharing connection, leading to a one dimensional, linear arrangement, as shown in Figure 2.8.^{35,87,89} The structure can be described as a hexagonal close packing, and is frequently referred to by its Ramsdell notation⁹⁰ of 2H, to distinguish it from other hexagonal polytypes, which are explained in the next paragraph. Inclusion of even larger organic cations can enable formation of these linearly arranged chains of lead halide octahedra as well,^{91–93} which is detailed in Section 9.3. The hexagonal structure is, in general, not desirable for photo-

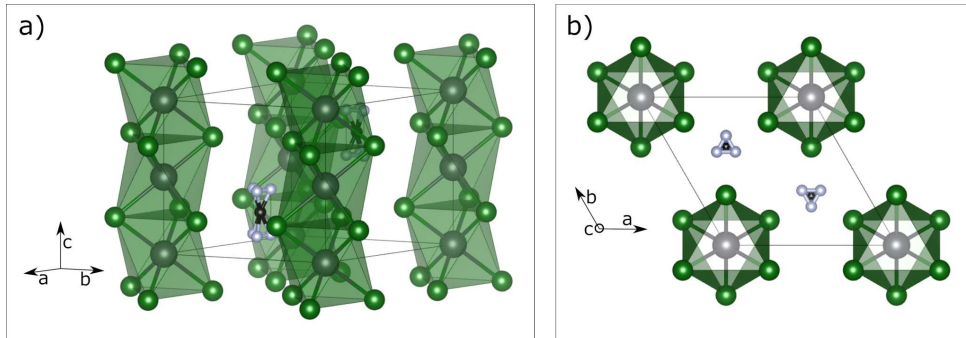


Figure 2.8: Crystal structure of the FAPbI_3 hexagonal δ -phase.⁸⁹ The view in (a) shows the 1-dimensional alignment of face-sharing lead halide octahedra, while the view along the c -axis in (b) highlights the hexagonal symmetry and disconnected nature of the lead halide substructure. Green spheres: iodide; large grey spheres: lead; black spheres: carbon; light slate blue spheres: nitrogen. Hydrogen atoms are omitted.

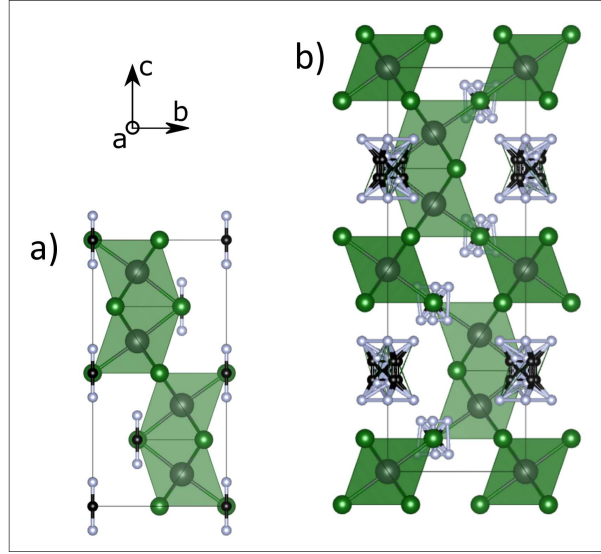
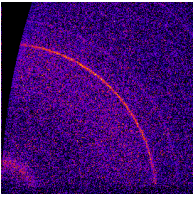


Figure 2.9: Crystal structures of the FAPbI_3 hexagonal polytypes.⁸⁹ (a) 4H, (b) 6H.⁹⁰ The view along the a -axis highlights the different stacking sequences. Green spheres: iodide; large grey spheres: lead; black spheres: carbon; light slate blue spheres: nitrogen. Hydrogen atoms are omitted.

voltaic applications, since it leads to a structurally anisotropic material, which possesses a rather wide band gap, thus reducing the absorptive range.⁸⁷ Several methods can be applied to mitigate formation of the hexagonal phase in FAPbI_3 and favor perovskite phases instead,⁹⁴ a selection of which is presented below. However, the linear arrangement with high material anisotropy might be suited for different kinds of applications, where those anisotropic properties are desirable.

Hexagonal Polytypes Hexagonal polytypes are characterized by a different stacking sequence than the 2H δ -phase.⁸⁹ The structure is identical to the 2H phase along two dimensions, but varies in the third dimension, i.e. the stacking sequence. Alternate stacking of the lead halide octahedra in the corner and face-sharing motifs leads to stacking sequences with 4-fold and 6-fold periodicity, these phases are named 4H and 6H, respectively. As depicted in Figure 2.9, while in 2H, the octahedra are purely face-sharing, in 4H and 6H the sequences consecutively increase in the proportion of corner-sharing octahedra. The 4H and 6H phases can therefore be viewed as intermediates between the 2H phase and the cubic perovskite phase. In this regard, a variety of stacking sequences featuring corner-sharing as well as face-sharing lead halide octahedra are realized, creating larger stacking sequences such as 8H, 10H, and beyond.^{95,96}

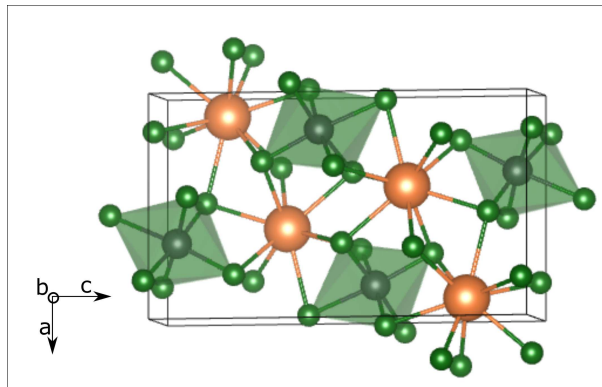
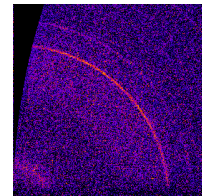
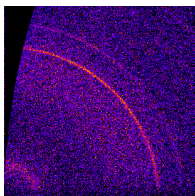


Figure 2.10: Crystal structure of the CsPbI_3 orthorhombic δ -phase.³⁵ Green spheres: iodine; large grey spheres: lead; large orange spheres: cesium.

Disconnected Structures Additional to the chain-like non-perovskite phases, featuring one dimensional chains of face sharing octahedra, disconnected structures have been observed as well, especially for fully inorganic materials, such as CsPbI_3 .^{35,97,98} Therein, the lead halide octahedra are not connected, but bridged via the cesium cation. The structure of the orthorhombic CsPbI_3 δ -phase is shown in Figure 2.10, where the disconnected lead halide octahedra are visualized. Such structures are, similar to the chain-like types, unfavorable for photovoltaic activity. Furthermore, large organic cations have been reported to form similar structures of disconnected octahedra with lead halides.⁹²



2.5 Solvent Complex Intermediates

During solution processing of perovskite materials, several different solvent complexes with the perovskite precursors play an important role.^{18,99–110} The most common and important of these solvent incorporating phases, which are able to form crystal structures, are briefly discussed in this section. Those intermediate phases in the process of perovskite formation can influence the final crystal structure in various ways, including templating effects for crystal orientation and symmetry. The type of solvent complex that is formed can depend on material stoichiometry as well as on the solvent itself. Since the different complexed phases exhibit different stabilities and therefore are expected to control the conversion speed into the perovskite phase during the annealing procedure, selecting a fabrication route with a suitable intermediate phase is crucial for optimization of the

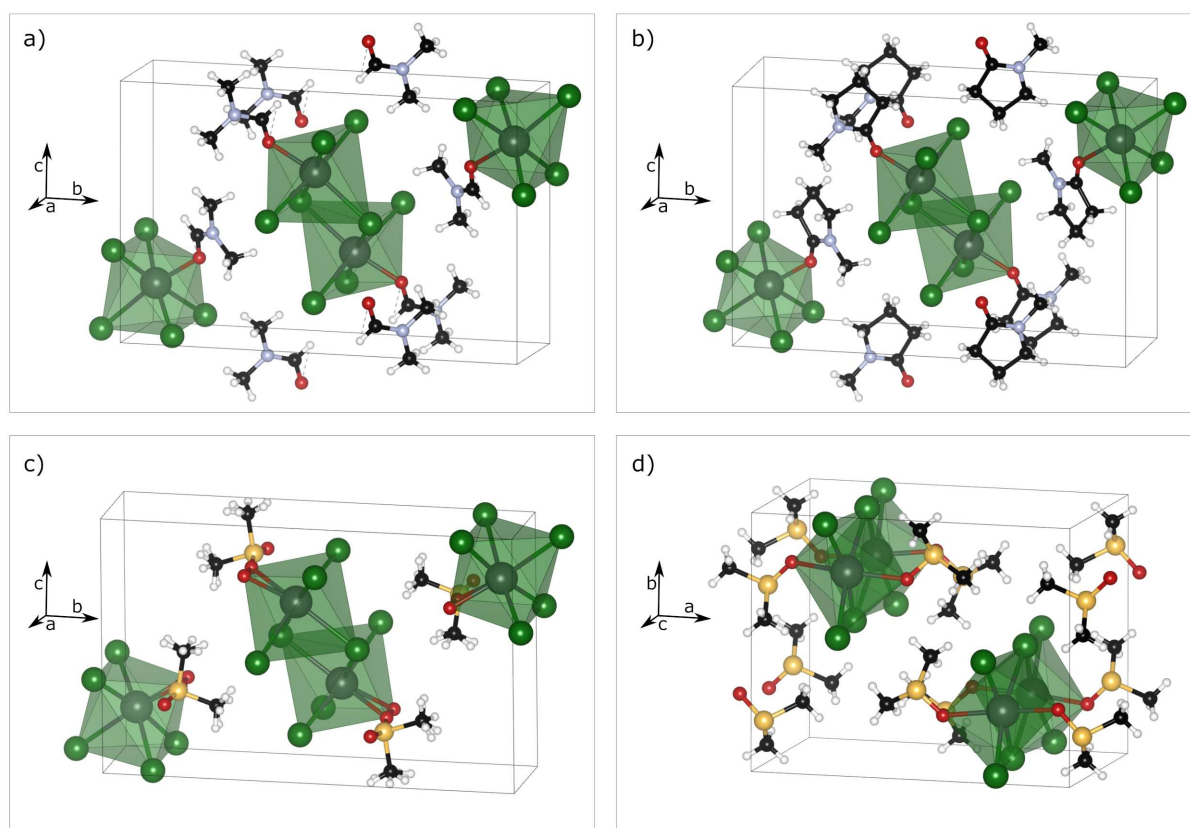


Figure 2.11: Crystal structures of crystalline solvent complexes of PbI_2 with commonly applied solvents for perovskite fabrication. (a) $\text{PbI}_2 \cdot \text{DMF}$;⁹⁹ (b) $\text{PbI}_2 \cdot \text{NMP}$;¹⁰⁰ (c) $\text{PbI}_2 \cdot \text{DMSO}$;¹⁰¹ (d) $\text{PbI}_2 \cdot 2\text{DMSO}$.¹⁰² Green spheres: iodide; large grey spheres: lead; black spheres: carbon; light slate blue spheres: nitrogen; red spheres: oxygen; yellow spheres: sulfur, smallest white spheres: hydrogen.

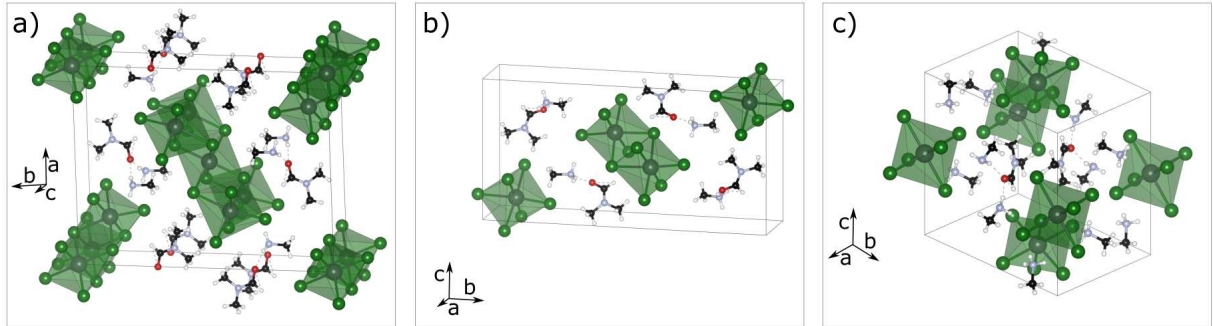
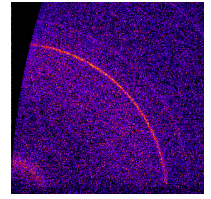


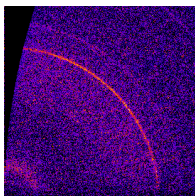
Figure 2.12: Crystal structures of crystalline solvent complexes of perovskite precursors with DMF.¹¹² (a) $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMF}$; (b) $\text{MA}_2\text{Pb}_2\text{I}_6 \cdot 2\text{DMF}$; (c) $\text{MA}_3\text{PbI}_5 \cdot \text{DMF}$. Green spheres: iodide; large grey spheres: lead; black spheres: carbon; light slate blue spheres: nitrogen; red spheres: oxygen.

crystal structure and morphology of the final material. Ultimately, there are coordinated structures containing only the solvent and lead iodide as well as structures containing the organic cations.

In sequential deposition processes, the solvent complexes with PbI_2 play a major role. The commonly applied solvents dimethylformamide (DMF), dimethylsulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP) have shown to form intercalated structures with PbI_2 . These structures are considered to be derived from the layered PbI_2 structure via introduction of the solvent molecules,¹⁰³ while rearranging the PbI_X octahedral building blocks into chain or ribbon-like linear arrangements.^{99, 101, 110, 111} Their structures are analogous to each other, comprising an equimolar stoichiometry of PbI_2 -solvent (with the solvent = DMF, DMSO or NMP, and shown in Figure 2.11 (a)–(c)). For DMSO, a second phase with the stoichiometry $\text{PbI}_2 \cdot 2\text{DMSO}$ has been observed as well,^{100, 102} as shown in Figure 2.11 (d). Both DMSO containing structures consist of chains of edge sharing PbI_5O octahedra, resembling fragments of PbI_2 stabilized by DMSO.¹⁰² NMP and DMF both were shown to form the equimolar structure only.^{99, 100}

In one-step-processes, where PbI_2 and methylammonium iodide (MAI) are present in the same solution, solvent complex formation behavior differs between the three solvents.

For DMF, three structures can be observed depending on the precursor stoichiometry.¹¹² With an equimolar ratio of MAI and PbI_2 , the stoichiometric structure $\text{MA}_2\text{Pb}_2\text{I}_6 \cdot 2\text{DMF}$ is formed. It consists of a ribbon-like motif of edge-sharing lead iodide octahedra. With an excess of methylammonium iodide, the MA-rich structure $\text{MA}_3\text{PbI}_5 \cdot \text{DMF}$ is formed, which features isolated corner-sharing chains of octahedra. In addition, with a PbI_2 excess, formation of an iodide-rich $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMF}$ phase has been observed, where a similar



2.5. SOLVENT COMPLEX INTERMEDIATES

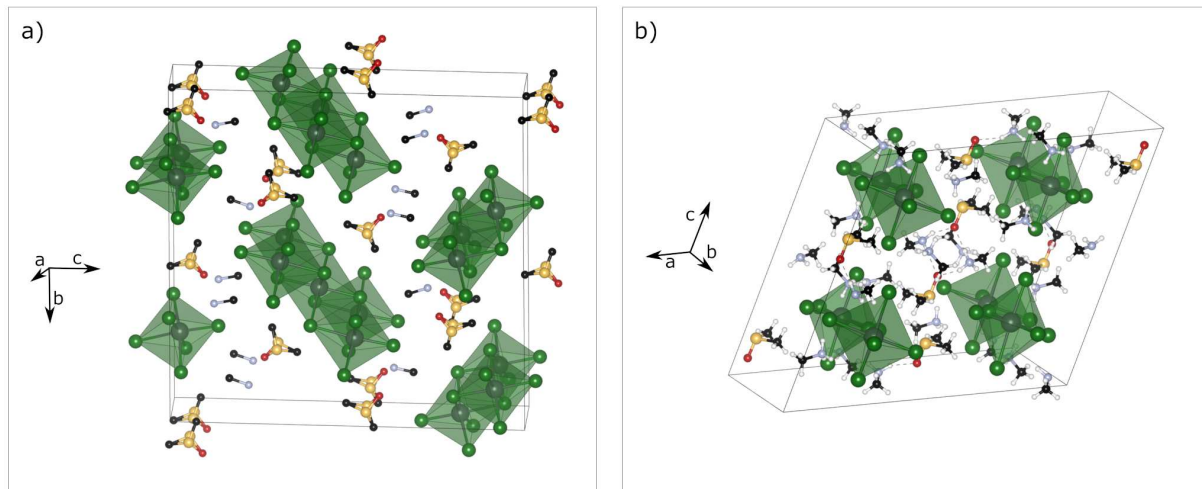
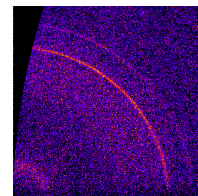


Figure 2.13: Crystal structures of crystalline solvent complexes of perovskite precursors with DMSO. (a) $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$,¹⁰¹ (b) $\text{MA}_3\text{PbI}_5 \cdot \text{DMSO}$.¹⁰² Green spheres: iodide; large grey spheres: lead; black spheres: carbon; light slate blue spheres: nitrogen; red spheres: oxygen; yellow spheres: sulfur.

ribbon-like motif of edge-sharing lead iodide octahedra as in the equimolar complex is found, however here with triple ribbons. The structures are shown in Figure 2.12. The stoichiometric $\text{MA}_2\text{Pb}_2\text{I}_6 \cdot 2\text{DMF}$ intermediate, sometimes written as $\text{MAPbI}_3 \cdot \text{DMF}$, can be fabricated by exposure of the $\text{PbI}_2 \cdot \text{DMF}$ structure to MAI as well.¹⁰¹ Likewise, compositions containing the FA^+ ion can form equimolar solvent complexes with DMF, resulting in a $\text{FAPbI}_3 \cdot \text{DMF}$ structure similar to the MA^+ -based analogue. In addition, a solvent-rich $\text{FAPbI}_3 \cdot 2\text{DMF}$ structure was observed,¹¹³ which can be attributed to the ability of formamidinium to form additional hydrogen bonds to link two DMF molecules.¹⁰⁶ Furthermore, an iodide-rich phase of $\text{FA}_2\text{Pb}_3\text{I}_8 \cdot 4\text{DMF}$ was observed in $\text{FA}^+ \text{-Cs}^+$ perovskite precursor mixtures along with an analogous $\text{Cs}_2\text{Pb}_3\text{I}_8 \cdot 4\text{DMF}$ phase.¹¹⁴

Due to the higher complexation strength of DMSO towards Pb(II) , the DMSO complexes have been observed to possess a higher stability than the DMF analogues. In a mixed-solvent solution, precipitation of the DMSO complexes is thus favored over DMF-based structures.^{112, 115} However, a stoichiometric solvent complex of MAPbI_3 with DMSO has not been observed, instead a $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ structure is formed directly from stoichiometric precursor solutions¹⁰² as well as from exposure of $\text{PbI}_2 \cdot X\text{DMSO}$ ($X = 1, 2$) to MAI.¹⁰¹ The structure is similar to the DMF analogue and consists of ribbon like triple chains of edge sharing PbI_2 octahedra,^{102, 109} shown in Figure 2.13 (a). With MAI excess in the precursor solution, the MA-rich structures $\text{MA}_3\text{PbI}_5 \cdot \text{DMSO}$ (Figure 2.13 (b)) and MA_4PbI_6 have been observed. The former consists of isolated chains of corner-sharing



CHAPTER 2. STRUCTURES

octahedra, similar to the DMF analogue, but with a reduced symmetry, while the latter features individual PbI_6 octahedra.¹⁰² For compositions based on formamidinium, the formation of $\text{FAPbI}_3 \cdot \text{DMSO}$ adducts was proposed,^{116,117} while under certain circumstances for mixed formamidinium-cesium compositions, direct formation of hexagonal FAPbI_3 phases is observed.¹⁰⁵

With NMP, inclusion of methylammonium into solvent complexes was not reported yet, instead even in stoichiometric perovskite precursor solution, the $\text{PbI}_2 \cdot \text{NMP}$ structure was found to be favored.¹⁰⁵ However, for formamidinium, indications of $\text{FAPbI}_3 \cdot \text{NMP}$ complex formation have been reported.¹¹⁸

For bromide compositions, in general a direct perovskite crystallization is observed. An exception exists for lead deficient compositions containing formamidinium, where layered solvent adducts can be found. This behavior has been attributed to the critical role of hydrogen bonds between the FA^+ ion and bromide.¹⁰⁶ In mixed halide compositions of iodide and bromide, the solvate phases include only minor amounts of bromide, while parallel crystallization of a bromide-rich perovskite is found.¹⁰⁶

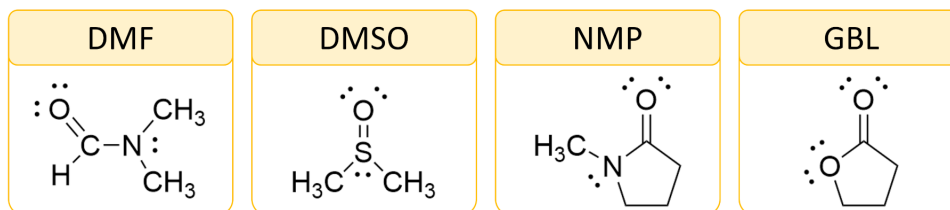
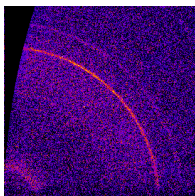


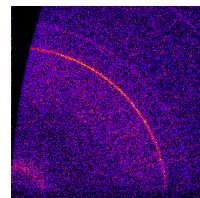
Figure 2.14: Molecular formulae of the commonly employed solvents for perovskite precursors, dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and γ -butyrolactone (GBL).

To rationalize the formation of crystalline solvent including intermediates, it is conducive to consider the interactions and complex formation already in the precursor solution. Thereby, donor and acceptor abilities of the involved species are taken into account. The coordination ability of a given solvent with Pb(II) correlates to the stability of the perovskite precursor solvent complexes, which decreases in the order of $\text{DMSO} > \text{DMF} > \text{NMP} > \text{GBL}$ for the most commonly utilized solvents in perovskite synthesis.^{119,120} Their molecular structures are shown in Figure 2.14. These solvents are expected to act as Lewis bases (electron donors) in coordinating the Lewis acidic (electron accepting) Pb(II) cation.¹¹⁸ As a measure of coordination ability, Gutmann's donor number is widely applied,¹²¹ additionally the sterical accessibility of the electron donating atom has to be considered.¹¹⁸ A strong affinity of the solvent to Pb(II) leads to the



2.5. SOLVENT COMPLEX INTERMEDIATES

formation of solvated species, whereas a low or medium affinity favors the formation of higher order polynuclear iodoplumbates.^{122–124} To dissolve perovskite precursors, highly polar aprotic solvents are required.¹²⁵ Due to the competition between halide ions and solvent molecules for the lead complexation, the formation of species coordinating higher numbers of iodide must still be permitted in order to facilitate subsequent perovskite formation.¹²⁶ Thus, partially solvent coordinated iodoplumbates already form in the precursor solution, which can predetermine the nature of crystalline intermediates during thin film deposition.¹²³



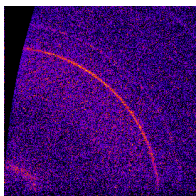
Chapter 3

Composition Dependent Properties of Perovskite Materials

This chapter elucidates further on the special properties of hybrid perovskite materials, including a variety of compositions and structures, covering the effects of mixing the different types of components as well. In the first section, general material properties are explained, followed by several sections focusing on each of the ion types adopting the different positions of the perovskite structure: organic (or inorganic) central cation and the halide, while the metal cation is featured in Section 5.1. Special properties of layered structures are covered afterwards and finally the mixed dimensional compositions are addressed.

3.1 General Properties

The primary hybrid perovskite material, which was employed in the seminal work of Miyasaka *et al.*,¹ and still is one of the most widely investigated of all perovskite compositions, is methylammonium lead iodide, MAPbI_3 .¹²⁷ It has shown many peculiar material properties in itself, which are, in considerable parts, due to its hybrid nature of organic and inorganic components, leading to a wide range of interactions within the material. The organic cation strongly influences the unique material properties,⁴⁶ due to its asymmetry and permanent dipole moment. Thereby, it can exert a strong influence on the electronic system and contribute to the dielectric response and the ferroelectric behavior.^{128,129} The molecular cation is prone to external manipulation, such as heat, light or electric fields, affecting the molecular dynamics inside the perovskite.⁴ Considerable thermally activated motion is observed for the MA^+ cation, including rotation and migration within



3.1. GENERAL PROPERTIES

the crystal lattice, which respectively occur on different time scales.¹³⁰ Single crystal analysis has shown that methylammonium is tumbling in its crystalline cages, while only the amine moiety interacts with the surrounding PbX_6 octahedra.¹³¹ This interaction distorts the iodide ions from their centrosymmetric positions, leading to a non-centrosymmetric crystal structure with anisotropic Pb-I distances and distorted angles, which allows for macroscopic polarization and ferroelectricity.⁴⁶

As a non-excitonic material, the small exciton binding energy enables full ionization upon excitation by light, charge accumulation and suppressed charge carrier recombination.¹³² MAPbI_3 is considered to be a mixed ionic-electronic conductor due to the facile vacancy assisted migration of iodide ions, whereby the levels of intrinsic iodide vacancies influence the iodide conduction.^{130,133} The ionic charge transport character is considered to be partly responsible for the observed hysteresis in current-voltage characteristics. The drift and diffusion of large electron/hole polarons, including the transport of charged ionic defects creates a complex charge transport process, which exceeds the scope of simple drift-diffusion models.¹³⁰

Materials characterization is sensitive to time and length scales of the measurement as well as the history of the sample¹³⁴ since large variations between the local and average crystal structure have been found.¹³⁰ Besides that, the morphology of the thin films and grains affects the material properties.^{4,135,136} Phase transitions are to be taken into account as well, with the most common perovskite materials, their phases and transition temperatures shown in Table 3.1. Figure 3.1 illustrates the room temperature stable phases for different compositions in relation to their tolerance factor.

MAPbI_3 adopts a tetragonal phase at room temperature, which transforms to a cubic structure at about 57°C .¹³¹ While some phase transitions can exert distinct effects on the material properties, as described further below, the tetragonal-cubic phase transition exerts only minor effects on the optoelectronic properties of MAPbI_3 . The local structure of edge-sharing lead halide octahedra is retained during the transition (compare Section 2.2), which is considered to primarily determine the optoelectronic properties.⁷⁰

The occurrence of phase transitions between different (distorted) perovskite phases is mostly a function of temperature. Notably, the highest symmetry high temperature structure usually possesses the most favorable properties for optoelectronic applications.³⁵ However, due to the hybrid nature of these perovskite materials, their thermal stability is rather low. MAPbI_3 has been observed to fully decompose starting at 150°C ,¹³⁷ while showing signs of degradation already at much lower temperatures.¹³⁸ Formamidinium-based materials possess a slightly higher heat tolerance,^{37,139} which can be considerably increased even more within all-inorganic materials such as CsPbI_3 .^{140,141}

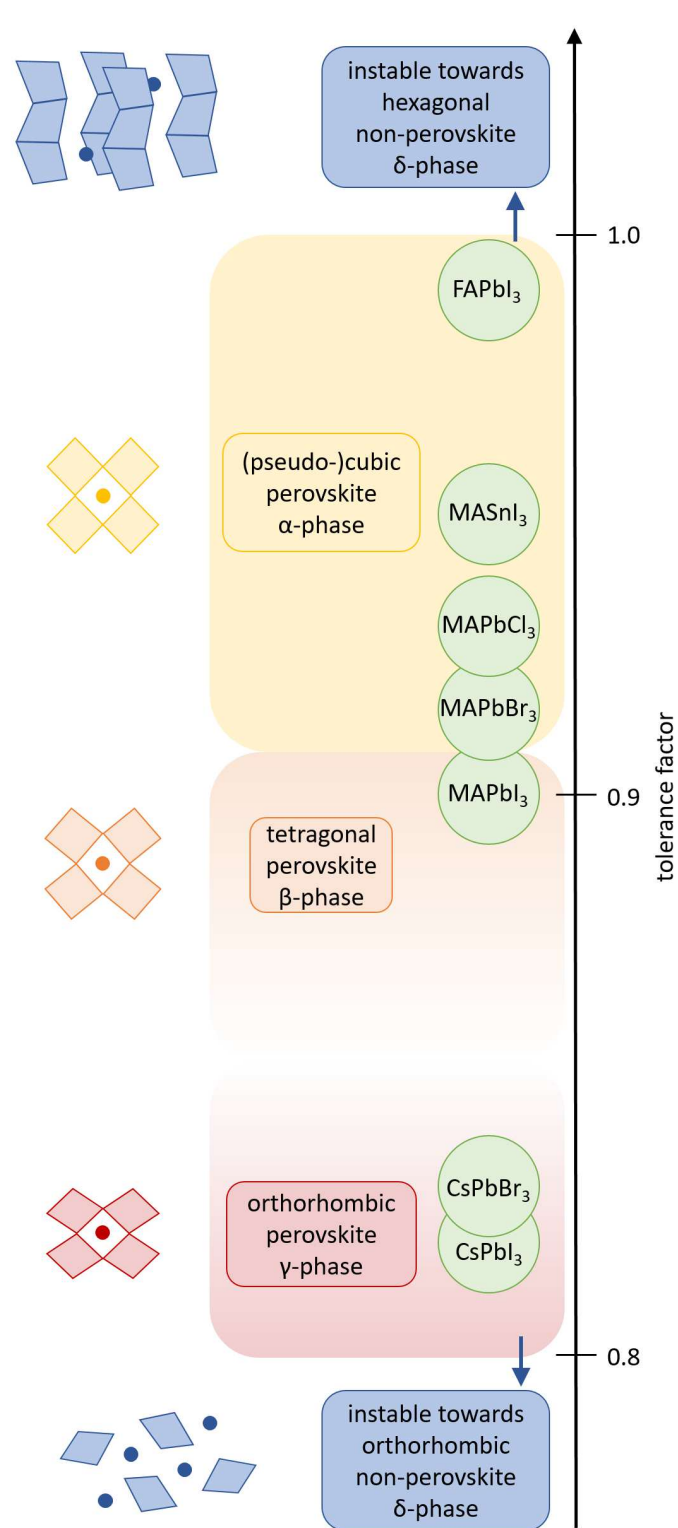
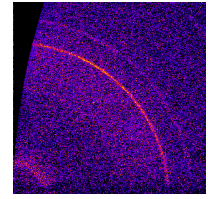
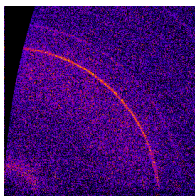
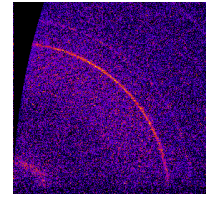


Figure 3.1: Stable phases at room temperature for different perovskite compositions as a function of the tolerance factor (see Section 2.1).



Thus, despite the MAPbI_3 perovskite exhibiting many special and intriguing properties itself, one of the main assets of perovskite materials is their large variety in composition as well as miscibility of ions, creating an even greater compositional space. Figure 3.2 depicts the most employed components for hybrid perovskites in the context of solar cell research. The following sections explore changing and mixing the different components, starting with the organic cation, followed by the halide. For perovskite component candidates, considerations such as tolerance factors, solvent compatibilities and the ability to form photoinactive phases have to be taken into account.¹⁴² As the organic, or rather ‘central’, cation, besides methylammonium, formamidinium has been extensively explored as well as inorganic cations such as cesium and rubidium.^{37, 87, 143–147} The most widely applied halides are iodide, bromide and chloride. Alternative anions, such as BF_4^- , SCN^- and PF_6^- , are subject to investigation as well.^{148, 149} The metal cation, which in most compositions is lead, might possibly be replaced by related metals, which is discussed in section 5.1.



3.2 Changing the Central Cation

Many of the perovskites' unique properties are governed by the central organic cation. Methylammonium is applied as the most widespread organic cation for hybrid perovskites, which in itself is responsible for several of the special material properties as covered in the previous section, many of those depending on the molecular dynamics.

Those dynamics are implied to be at least partially faster when exchanging methylammonium for formamidinium (FA^+).^{150, 151} Reorientation dynamics have shown to correlate with carrier lifetimes, due to the polaronic nature of the charge carriers.¹⁵⁰ Thus, lifetimes increase when introducing formamidinium ions.

Incorporating the larger formamidinium ion instead of methylammonium increases the lattice parameter of the perovskite structure, which in turn reduces the band gap,^{37, 87, 152} allowing for a slightly broader absorption range. However, due to an increase of the tolerance factor caused by the larger ionic radius, the most stable phase for FAPbI_3 at room temperature is the yellow non-perovskite δ -phase, which is unsuited for photovoltaic applications.^{35, 87} Although pure FAPbI_3 can be prepared in a (pseudo-)cubic perovskite phase, it is unstable under ambient conditions and tends to transform into the δ -phase,

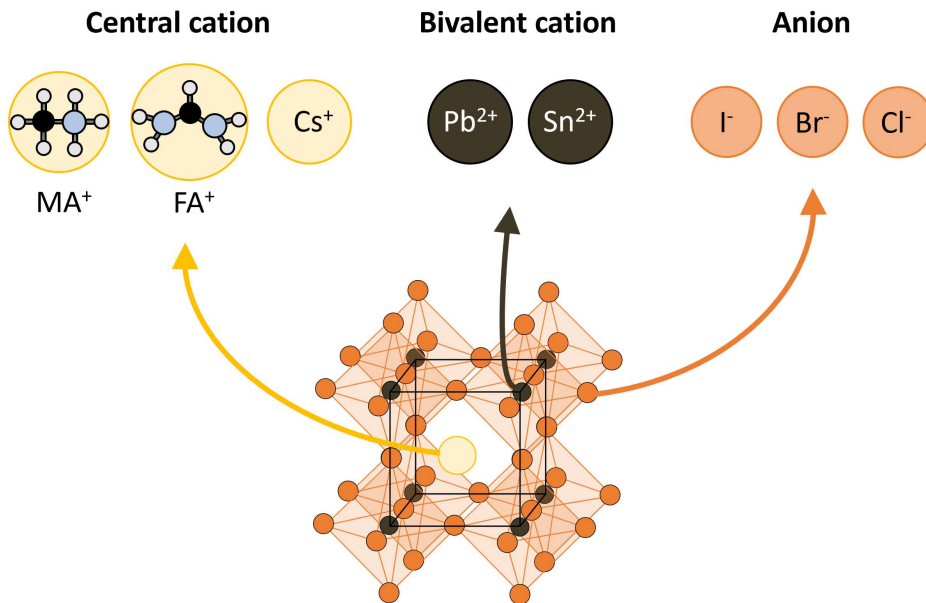
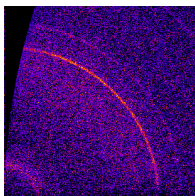


Figure 3.2: Schematic representation of the most widely employed components for mixed-material perovskite compositions. MA^+ = methylammonium, FA^+ = formamidinium; within their molecular structures, black circles represent carbon, blue spheres represent nitrogen and white spheres depict hydrogen.



3.2. CHANGING THE CENTRAL CATION

especially when triggered by environmental influences such as moisture.⁸⁷

Cation mixing has been established as a possibility to stabilize the FAPbI₃ perovskite phase at room temperature, which is described below and featured in detail in Section 9.1. The resulting pseudo-cubic α -polymorph is metastable at room temperature, while a tetragonal phase, similar to the MAPbI₃ analogue is exhibited between -133°C and 12°C . Below -133°C , no clear unit cell and no supercell can be observed, indicating a locally disordered low temperature γ -phase.^{35,64,65} Entropy contributions have shown to play an important role in the phase transitions, especially from the cubic to the hexagonal phase. In addition, a large thermal hysteresis, due to a potential barrier between the phases is observed. Thus, kinetic trapping of the cubic phase is possible by thermal quenching.¹⁵³ A similar hexagonal non-perovskite phase has been predicted for MAPbI₃, which is isostructural to δ -FAPbI₃,¹⁵⁴ but is not readily observed, except under drastic conditions such as an extensive excess of MAI.¹⁵⁵

Inorganic Cations As an alternative to the organic cations, which are often prone to degradation,^{138,157–161} inorganic cations of appropriate size and charge can be applied as a central cation as well. The most commonly applied metal cation is cesium, which can form a perovskite structure with lead and tin halides.^{162–164} All-inorganic halide perovskite materials have shown improved environmental stability, but lower power conversion efficiencies and phase instability.¹⁶³ In general, the electronic and optical properties of Cs-based materials have been reported as quite similar to their counterparts based on methylammonium, but structures and ferroelectric properties can differ.¹⁶⁵ This is considered to be related to the spherical symmetry of the single atom cesium cation, which the methylammonium cation does not possess.

For CsPbI₃, the room temperature photoactive phase is the orthorhombic γ -polytype of the perovskite structure.^{97,166} However, this phase has shown to be metastable and prone to forming an orthorhombic non-perovskite δ -phase.¹⁶⁷ Heating converts the material into the cubic perovskite α -phase, but upon cooling it is converted back via β and γ -phases.⁹⁷ A similar behavior is found for CsPbBr₃.^{67,162} To stabilize the perovskite phase at room temperature, as for the organic cations, cation mixing is a possible route.

Cation Mixing Mixing cations has proven to be an effective way of stabilizing the photoactive perovskite structure as well as tuning material properties. While mixing the organic cations FA⁺ and MA⁺ to stabilize FAPbI₃-rich perovskite phases is a widespread approach, especially formamidinium and cesium cations have shown to be good alloy partners, stabilizing each other's perovskite phases.^{168,169} For FAPbI₃, the tolerance factor is

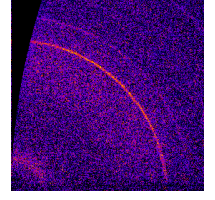
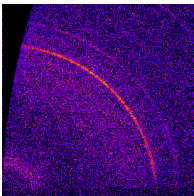


Table 3.1: Phases, crystal symmetries and stable temperature ranges for common hybrid perovskite compositions.

Material	Phase	Symmetry	Temperature Range	Reference
MAPbI₃	α	(pseudo-)cubic	$> 57^\circ\text{C}$	[62, 63]
	β	tetragonal	$-112\dots 57^\circ\text{C}$	
	γ	orthorhombic	$< -112^\circ\text{C}$	
	δ	hexagonal		[154]
FAPbI₃	α	(pseudo-)cubic	$> 12^\circ\text{C}$ (stable $> 87^\circ\text{C}$)	[64, 151]
	β	tetragonal	$-133\dots 12^\circ\text{C}$	[64, 65]
	γ	locally disordered	$< -133^\circ\text{C}$	
	δ	hexagonal	$< 87^\circ\text{C}$	[35, 87]
CsPbI₃	α	cubic	$> 260^\circ\text{C}$	[68]
	β	tetragonal	$175\dots 260^\circ\text{C}$	
	γ	orthorhombic	$< 175^\circ\text{C}$	
	δ	orthorhombic	$< 360^\circ\text{C}$	
MAPbBr₃	α	cubic	$> -37^\circ\text{C}$	[60, 61]
	β	tetragonal	$-118\dots -37^\circ\text{C}$	
	γ	tetragonal	$-124\dots -118^\circ\text{C}$	
	δ	orthorhombic	$< -124^\circ\text{C}$	
CsPbBr₃	α	cubic	$> 130^\circ\text{C}$	[66, 67]
	β	tetragonal	$88\dots 130^\circ\text{C}$	
	γ	orthorhombic	$< 88^\circ\text{C}$	
	δ	orthorhombic	$< 130^\circ\text{C}$	[156]
MAPbCl₃	α	cubic	$> -96^\circ\text{C}$	[60, 61]
	β	tetragonal	$-101\dots -96^\circ\text{C}$	
	γ	orthorhombic	$< -101^\circ\text{C}$	



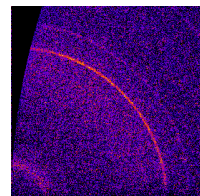
3.2. CHANGING THE CENTRAL CATION

rather high, favoring a hexagonal δ -phase, while for CsPbI_3 , the smaller tolerance factor favors an orthorhombic δ -phase.¹⁶⁸ Mixing both together, the effective tolerance factor can be tuned, resulting in an overall stabilization of the photoactive perovskite α -phase. This is due to the fact that the δ -phases of FAPbI_3 and CsPbI_3 are immiscible, but mixing is favorable in the perovskite phase, leading to entropic stabilization.¹⁶⁹

More fine tuning can be achieved when applying three cations (MA^+ , FA^+ , Cs^+).¹⁷⁰ Stabilizing the photoactive FAPbI_3 -phase by adding MA^+ or Cs^+ ions leads to a tetragonal (pseudo-cubic) phase with a small degree of octahedral tilting, which effectively frustrates transition to the hexagonal phase.¹⁷¹ Additionally, the transition temperature to the FAPbI_3 α -phase is reduced by mixing with MA^+ , Cs^+ or Rb^+ , showing a lower energy difference between δ and α -phase,^{144,145} due to the structural distortion induced by adding smaller cations.⁵⁶ The optical and electronic properties, however, are only slightly affected by cation mixing, although the band gap can be tuned via the mixing ratio.^{56,172} Optimal photovoltaic properties for FA:MA mixtures have been established at about 15 % of MAPbBr_3 .^{173,174}

Including cesium and rubidium cations has shown to improve the photovoltaic performance of perovskite solar cells,^{144–147,175} notwithstanding that the question whether or not the smaller rubidium cation is actually included into the perovskite structure has been debated heavily in literature.^{144,145,147,172,175–178} Cations smaller than rubidium, such as potassium, have likewise been investigated to possibly be added into perovskite formulations. These experiments did not result in successful incorporation into one of the common mixed perovskite structures yet.^{179–183}

Mixing cations, including FA^+ , MA^+ , Cs^+ and Rb^+ is the main subject of publication [I] and is thus elucidated further in Section 9.1.



3.3 Influence of the Halide

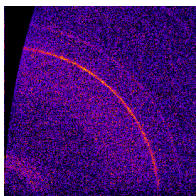
Besides cation mixing, mixing the halides in hybrid metal halide perovskite compositions has been widely applied to tune the material properties.^{36,184} Especially for band gap tuning, mixing iodide and bromide, in some cases even chloride, is a viable route, allowing to create materials with band gaps between 1.48 and 2.35 eV.^{184,185} The larger the halide ion is, the larger the lattice parameter, which in turn leads to a decrease of the band gap.¹⁵² Mixing different halides leads to a behavior of lattice parameter and band gap following Vegard's law,¹⁸⁶ making nearly continuous tuning possible.

In addition to the optoelectronic properties, phase and material stability are influenced by the choice of halide as well. In methylammonium lead halides, MAPbX_3 , while the iodide component exhibits a tetragonal structure at room temperature, bromide and chloride form a cubic perovskite.¹³¹ The sensitivity to degrading factors such as light, heat or temperature can strongly depend on the choice of halide. The combination of light and heat can readily degrade MAPbI_3 , while MAPbBr_3 remains stable under the same conditions.^{158,161} This is considered to be due to differences in bond strength, which has been reported to be higher for the Pb–Br bond than the iodide counterpart¹⁸⁷ and differences in the crystal structure since the cubic MAPbBr_3 is sterically denser than the tetragonal MAPbI_3 and thus less prone to attacks by external species driving degradation.¹⁵⁸

Halide Segregation As mentioned above, halide mixing, in most cases iodide and bromide, has been widely investigated to adjust band gaps to certain desired values, which, for example, can be optimized for tandem applications. However, in these mixed halide perovskites, a reversible phase separation into iodide-rich and bromide-rich phases has been observed upon injection of charge carriers, both directly^{188,189} and via illumination.¹⁹⁰ This can be detrimental for applications by creation of low-band gap domains.^{191,192} Thus, band gap tuning is essentially revoked, which potentially leads to creation of charge extraction barriers as well.¹⁹³

To explain the phenomenon, several mechanisms have been proposed, including thermodynamic models,^{194,195} polaronic strain models,^{192,196,197} redox reactions,¹⁹⁸ emergence of internal electric fields due to carrier trapping,^{199,200} and various combinations of these.^{201–204} So far, other than the fact that charge carriers, which can be induced via illumination of the photovoltaically active material, play an integral role,²⁰⁵ there is no consensus on the exact separation mechanism.

The question whether defects such as grain boundaries and surfaces are required for phase segregation or if halide segregation is an intrinsic material property is a matter of



3.3. INFLUENCE OF THE HALIDE

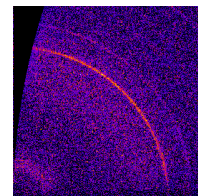
ongoing research.^{196,206–208} A stochastic nucleation of iodide-enriched domains has been reported,^{196,209,210} pointing towards halide segregation as an intrinsic material property. Notably, a preferred occurrence of halide segregation in defect-rich materials^{206,211–215} and near grain boundaries²⁰⁷ has been found as well, which at least accounts for them as possible promoting factors. The mixed state is considered to segregate into regions enriched in both halides separately upon excitation of the material due to its metastability.²¹⁶ Different extents of the miscibility gap have been predicted by different models.^{194,195} Charge carriers can be funneled into iodide-rich regions^{191,193,194,216,217} (or more general, regions rich in the larger halide in the mixture), due to their slightly lower band gap compared to the surrounding material, making them preferred centers of recombination.^{209,217–219} Thus, this process is enhanced by any compositional inhomogeneities that are present in the material, whereby iodide-rich regions can act as nucleation centers for further encouraging ongoing phase segregation.^{194,201,216,218,219} Therefore, for mitigating halide segregation, a homogeneous composition throughout the material and high crystal quality is assumed to be beneficial.^{216,220,221}

Remixing in the dark is considered to be entropically driven.^{195,222–225} Notably, mixed halide $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ material can also be created by heating a physical mixture of MAPbI_3 and MAPbBr_3 powders,²²⁶ which indicates a beneficial effect of either thermal energy or entropy contributions on halide mixing.

The greatest tendency for halide-segregation is exhibited by methylammonium-based materials, while FA-Cs based structures are considered to be more stable.^{188,192,216,220,227–229} Partial substitution of lead with tin has been reported to mitigate halide segregation as well,²³⁰ further highlighting the intertwined nature of the influences of the different components in a perovskite composition.

Contrary to bromide, which is at least miscible into MAPbI_3 -based perovskite formulations under the right conditions, for mixing chloride and iodide in methylammonium-based perovskites, a broad miscibility gap has been reported.^{231,232} MACl is widely applied as a supportive agent for MAPbI_3 crystallization, but is assumed to be lost during annealing and not incorporated into the perovskite structure.²³²

Halide mixing and halide segregation of mixed iodide-bromide perovskites, focusing on the crystallization and growth of these materials is explored in Section 9.4.



3.4 Layered Perovskite Materials

Many hybrid perovskite materials have shown poor stability against environmental humidity. For mitigation of this instability, layered materials, the 2D-perovskites containing larger, more hydrophobic molecular cations, are a possible utility.²³³ Their structures are described in Section 2.3. Due to the water-repulsive properties of these larger spacer cations, such as aromatic and aliphatic hydrocarbon amines, the stability of these materials against humidity^{75,85,234–238} as well as general durability is increased.^{75,239} In comparison to their smaller counterparts employed for 3D perovskite structures, larger organic cations exhibit lower ionic mobility, are less volatile and offer further chemically active sites. All these assets are considered beneficial for material stability and functionality.²⁴⁰

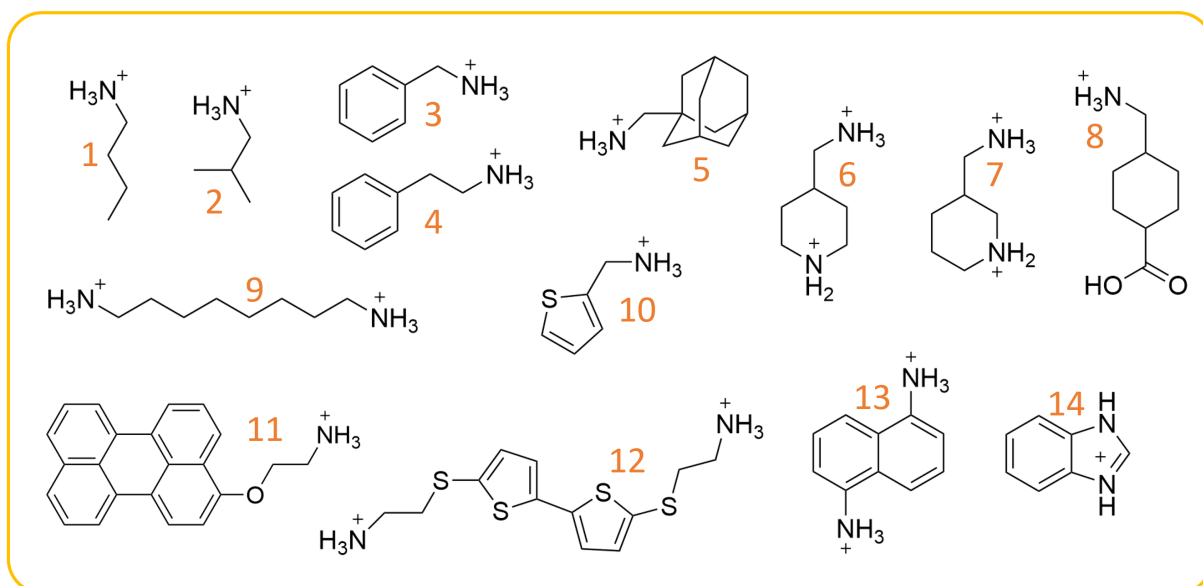
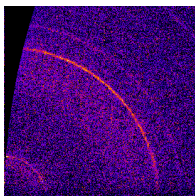


Figure 3.3: Examples for molecular spacer cations which can be used in layered perovskite structures, showing a small excerpt of the large variety of spacers. (1) butylammonium (BA^+),^{78,79,241} (2) iso-butylammonium (iBA^+),^{242,243} (3) benzylammonium (BNA^+),^{76,244–246} (4) phenylethylammonium (PEA^+),^{236,247} (5) (1-adamantyl)methylammonium (ADAM^+),²⁴⁸ (6) 4-(aminomethyl)piperidinium (4-AMP),⁸² (7) 3-(aminomethyl)piperidinium (3-AMP),⁸² (8) (carboxy)cyclohexylmethylammonium,²⁴⁹ (9) octyldiammonium,²⁵⁰ (10) 2-thienylmethylammonium,²⁵¹ (11) perylene-O-ethylammonium,²⁵² (12) 5,5'-bis(ammoniummethylsulfanyl)-2,2'-bithiophene,²⁵³ (13) 1,5-diammoniumnaphthalene,²⁵⁰ (14) benzimidazolium.²⁵⁴



3.4. LAYERED PEROVSKITE MATERIALS

As introduced in Section 2.3, mono or bifunctional molecular cations can be applied to form bilayers or monolayers of the organic spacers, respectively. Examples of possible spacer cations for layered perovskitoid materials are depicted in Figure 3.3. The main requirements for molecular cations to be applicable as a spacer are the presence of a terminal cation moiety to interact with the lead halide network and a small enough cross-section to fit into the perovskite structure. Furthermore, favorable interactions or at least no repulsions between side groups are essential, so that the spacers can be packed accordingly.^{45,75} The length, geometry and further functionalization of the spacer cations is greatly variable.⁷⁵ This enables a vast potential for chemical functionalization of the spacers to generate and tune specific molecular and material properties^{73,75} as well as facilitate self-assembly of the structures.^{75,237,240} In general, the chemical properties of the resulting materials, such as solubility, thermal stability, hydrophobicity or crystallinity are mainly governed by the organic spacer cations, while the inorganic layer mainly defines the optical and electronic properties.⁷⁵ Beyond that, the influences of all components are highly intertwined since conformation and ordering of the molecular cations can induce distortions in the inorganic layers and vice versa.^{48,82,85,255}

The resulting structure types show a distinct anisotropy in their optoelectronic properties due to their layered nature, as schematically depicted in Figure 3.4. Charge transport

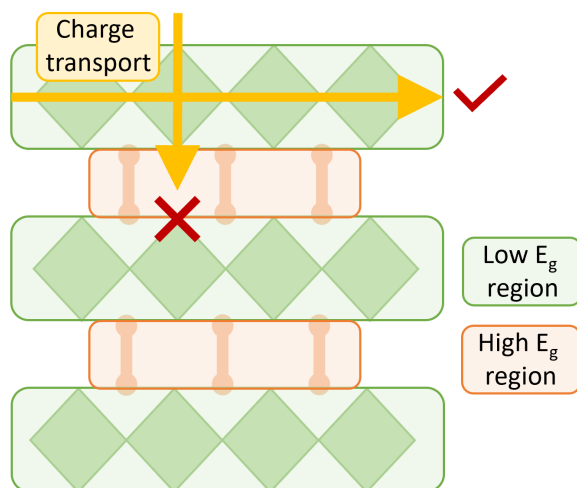
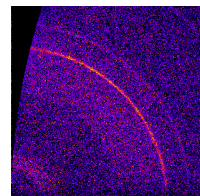


Figure 3.4: Schematic representation of the intrinsic quantum well structure of layered perovskites. Green shaded regions with squares indicate the inorganic lead halide layers, orange regions with dumbbell shapes depict the organic spacer layers. Yellow arrows indicate directions where charge transport is possible along the layer direction and hindered in perpendicular direction.



CHAPTER 3. PROPERTIES

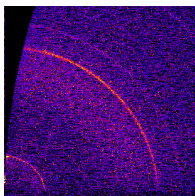
is blocked in perpendicular direction to the layer planes, but possible along the layer direction.²³⁵ An intrinsic quantum well structure is established,²⁵⁶ where the thickness of the quantum well can be adjusted by the composition of the material to form perovskite slabs of different layer thickness n , as shown in Section 2.3. Changing n , the material properties can be adjusted as well, as described below. Generally, reducing the dimensionality of the structure increases the binding energy and band gap, which can thus be tuned by the composition.^{235, 255} An increased band gap, strongly bound excitons, low charge carrier mobilities as well as dielectric mismatch of the organic and inorganic layers render 2D perovskites rather unsuitable to be applied as solar cell absorbers on their own.^{75, 236, 257} Their quantum well structure, however, enables different kinds of applications such as LEDs^{73, 258} or transistors.²⁵⁹ Thereby, the layer number n determines quantum well width, while the length of the spacer cation along its long molecular axis determines the barrier thickness.^{237, 255} A reduced distance between the inorganic layers can facilitate the charge transport and improve material stability.²⁶⁰

Thus, choice of the molecular spacer is key to obtain structures with the respective beneficial properties for the desired applications. As introduced in Section 2.3, the ionic functionality (mono or bifunctional) determines whether a bilayered Ruddlesden-Popper type of structure or a monolayered Dion-Jacobson type of structure is obtained, both of which exhibit their specific peculiarities.

Ruddlesden-Popper Phases As introduced in Section 2.3, Ruddlesden-Popper (RP) phases are based on bilayers of monofunctional spacer cations. This renders them the most flexible type of 2D structure⁸² due to the relatively weak van-der-Waals forces connecting the bilayer²³⁷ and the possibility for the spacers to adopt different configurations and packing patterns, exposing them to a larger amount of intrinsic disorder.^{73, 261}

Commonly applied molecular spacers include aliphatic and aromatic primary ammonium cations, such as butylammonium,^{78, 79, 241} phenylethylammonium^{236, 247} or benzylammonium.^{76, 244–246} Beyond, a variety of bulky molecular cations such as adamantyl compounds,²⁴⁸ and many more have been investigated. One of the first spacer cations for RP phases, which is still one of the most widespread to this day, is phenylethylammonium (PEA^+). It is featured in Sections 11.4, 11.5 and 13, while the analogue with a shorter anchoring chain, benzylammonium (BNA^+) is discussed in Sections 11.4 and 11.5.

Dion-Jacobson Phases Dion-Jacobson (DJ) phases facilitate, compared to their RP counterparts, enhanced interactions between the inorganic layers, which generally leads to a reduced interlayer distance, increased structural stability and more facile interlayer



3.4. LAYERED PEROVSKITE MATERIALS

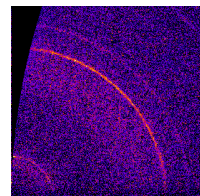
transport.^{82,262–264} This can suppress the quantum confinement effect of the layered structure, enabling charge separation to take place more efficiently than in other types of layered structures.²⁶⁵ Thus, DJ structures are the most promising type of layered structure for photovoltaic applications, especially in mixed dimensional architectures as presented in the next paragraph.

Dion-Jacobson types of materials are featured in Sections 11.1, 11.2 and 11.3.

Mixed Dimensions As mentioned previously, mixing large spacer cations with the smaller cations, which can form 3D perovskite structures, results in the formation of layered structures with a higher number n of inorganic lead halide layers between the spacer layers. Variation of the ratio of the small and large organic cations tunes the number n and therefore controls the effective dimensionality.⁴⁵ A higher n usually decreases the band gap since it reduces the quantum confinement in the lead halide layers as well as dimensionality effects.^{45,266}

In most cases, when attempting to create higher n layered structures, a mixture of phases with different n -values is obtained. This leads to mixed dimensional samples containing various layered phases and often 3D perovskite phase as well.^{104,233,267} This is considered to be caused by unfavorable formation enthalpies which have been determined for higher n structures.^{233,267,268} Those drive disproportionation of higher n compositions to lower n phases and a 3D perovskite phase.²⁶⁸ Generally, for solution-deposited thin films, the lower n phases are found predominantly in proximity to the substrate, while larger n and 3D phases tend to exist closer towards the film surface.^{104,237,238,269} Thus, a gradient structure of optoelectronic properties can be achieved, where carrier funneling can occur from higher to lower band gap regions.²⁷⁰

In order to retain the optoelectronic properties of the 3D-perovskite material and to exploit the stabilizing properties of the 2D-perovskite simultaneously, a 2D/3D structure can be fabricated. Therein, a thin film of the 2D-material is coated on top of an already existing film of 3D material.²⁷¹ This is a common technique to stabilize the surfaces of perovskite thin films, which can be applied inside device structures, as presented in Chapter 13.



Chapter 4

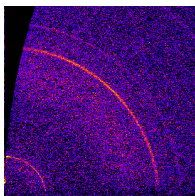
Thin Film Growth and Device Fabrication

So far, only the properties of ready-made perovskite materials and thin films have been described. Importantly, tuning and adjusting these already begins during thin film deposition and crystal growth. Thus, this chapter briefly introduces the growth and crystallization processes observed in perovskite thin films in Sections 4.1 and 4.2, respectively. Device structures and their fabrication are presented in Section 4.3.

4.1 Perovskite Thin Film Growth

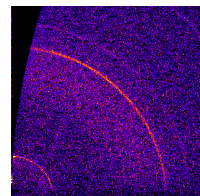
The growth and crystallization of the perovskite phase during deposition of thin films undergoes several stages that are frequently described by common models developed in crystallization theory.^{272,273} However, these models often fall short to explain the complex growth of perovskite thin films, which involves several different types of ions, solvent interactions and optional additives, leading to non-classical nucleation behaviors.^{274,275} This includes the presence of polynuclear haloplumbate complexes in perovskite precursor solutions, which can alter the nucleation and growth behavior^{122,276,277} as well as the formation of solvent complexes. Those can evolve into crystalline intermediate structures, introduced in Section 2.5, or a mixture thereof. Upon later stages of the deposition process, these intermediate structures are converted into the perovskite structure, as is described in the next section.

Controlling the drying kinetics of the as-deposited film via the solvent removal speed has been observed to heavily influence the final morphology of a perovskite thin film, and thus its applicability for utilization in devices.²⁷⁸ However, this is possibly only true to a



4.1. PEROVSKITE THIN FILM GROWTH

certain extent since, as is shown in Section 10.2, different crystallization rates can lead to similar thin film morphologies and grain sizes, while solvent additives can exert a much stronger effect on grain morphology than the crystallization kinetics. These additives, which are added into the precursor solution, are considered to influence nucleation and crystal growth, resulting in inducing crystallite orientation as well.^{279–284} A closer look at the effects of crystallization additives employing the example of thiourea is provided in Chapter 10, where evidence is shown that this additive exerts its effects in the final drying stage during thermal annealing irrespective of the crystallization kinetics.



4.2 Crystallization of Perovskite Phase

This section focuses on the crystallization pathways of perovskite thin films deposited from one-step solution-based processes. Since different perovskite components and precursors exhibit different bonding strengths towards solvent molecules, the type of intermediate, its conversion sequence into the perovskite structure as well as the formation and conversion rates depend on the composition of the precursor,^{285–287} as introduced in Section 2.5.

MAPbI₃ Perovskite Formation via Solvent Intermediate Structures Generally, the MAPbI₃ composition initially forms a crystalline solvent complex while spin-coating, the type of which depends on solvent and precursor ratios as described in Section 2.5. The solvent is thereafter liberated from the structure and evaporated by thermal annealing, converting the thin film into a MAPbI₃ perovskite^{109,288} as schematically depicted in Figure 4.1. The types of precursor solvate phases strongly impact the film morphology, device performance and reproducibility of the deposition. Similarly, the morphology of the precursor phase crystallites affects the perovskite phase crystallization and crystal quality.²⁸⁹ Precursors with higher crystalline order are more stable over time, thus more reproducible results can be obtained.²⁸⁸

Not only can the type of intermediate structure be influenced by the precursor ratio, but by carefully selecting the PbX₂ precursors as well. Therein, X can be a halide, acetate or nitrate, which can influence the precursor-to-perovskite transition and thereby quantify

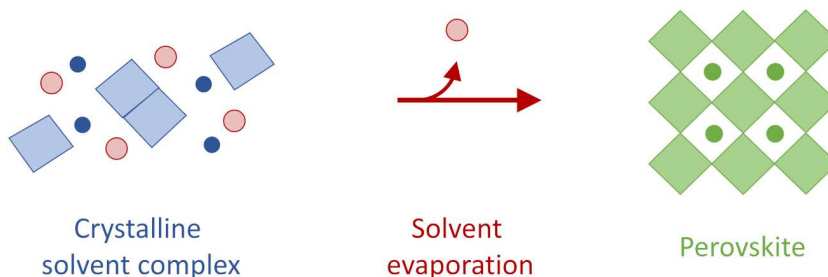
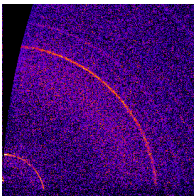


Figure 4.1: Schematic representation of the conversion of MAPbI₃ from a crystalline solvent complex into the perovskite phase. Notably, many different solvent complexes can exist as intermediate phases, which exhibit a variety of structures that are represented by one schematic example here. Blue and green quadrangles represent lead iodide octahedra, while full-colored blue and green circles represent methylammonium and the light-colored red circles represent the solvent molecules.



4.2. CRYSTALLIZATION OF PEROVSKITE PHASE

the degree of perovskite formation. The activation energy for the transition has been observed to strongly depend on the lead salt.²⁹⁰

FAPbI₃ Perovskite Formation via Hexagonal Polytypes Deposition of a FAPbI₃ composition results in initial formation of the hexagonal δ -phase, which requires conversion into the perovskite structure by thermal annealing.²⁹¹ This happens via the 4H and 6H phases as intermediates,⁸⁹ which were introduced in Section 2.4. These feature both the face-sharing lead halide octahedra of the hexagonal phase as well as corner sharing octahedra, which are characteristic for the perovskite phase. Since during the transition from the purely face-sharing to a purely corner-sharing structure, all of the lead halide octahedra require changing their connectivity, a number of intermediate stages is formed with different connectivities and stacking sequences. This starts with the 4H and 6H phases as depicted in Figure 4.2 and possibly includes lower-order or larger stacking sequences such as 8H and 10H,^{95,96} which eventually lead to formation of the cubic perovskite phase.

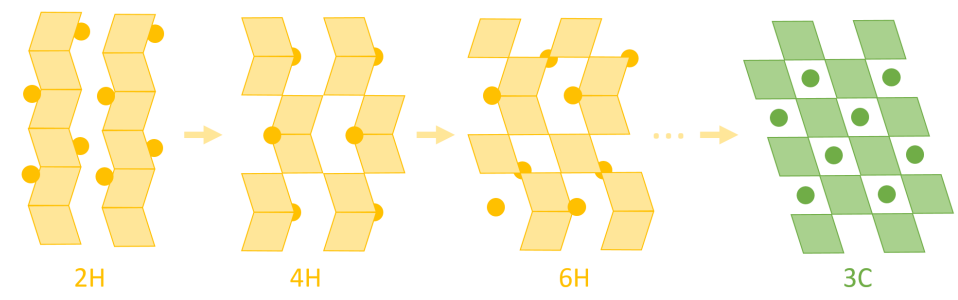
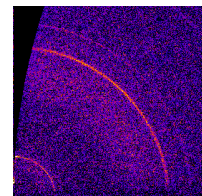


Figure 4.2: Schematic representation of the conversion sequence of FAPbI₃ from the 2H δ -phase into the cubic (3C) perovskite phase. An increasing amount of corner sharing lead iodide octahedra in expense of the face sharing structures following the sequence is visible as well as the characteristics of the 4H and 6H phases as intermediates between the 2H δ -phase and the perovskite.⁸⁹ Colored quadrangles represent lead iodide octahedra, while circles represent the formamidinium ions.

Perovskite Phase Formation in Mixed Compositions As introduced previously, perovskite materials are often fabricated applying mixed materials in order to stabilize the perovskite phase and tune the band gap energy. The crystallization sequence, however, is sensitive to the ion composition, and thus material mixing can contribute to tuning the crystallization behavior. The crystallization behavior of methylammonium-based mixed halide materials is discussed in Section 9.4.



CHAPTER 4. GROWTH & FABRICATION

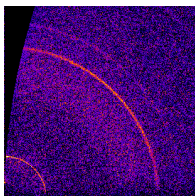
Mixed $(\text{FAPbI}_3)_x(\text{MAPbBr}_3)_{1-x}$ materials (where x is between 0 and 1), especially for higher FAPbI_3 proportions, crystallize in the hexagonal δ -phase first, similar to pure FAPbI_3 . The presence of bromide is considered to trigger the crystallization sequence via the hexagonal polymorphs.⁸⁹ Thus, upon deposition of mixed perovskite compositions, similar consecutive phase formation stages as for FAPbI_3 are observed. From the initial disordered precursor solution, the δ -phase forms, which then undergoes the transition described in the previous paragraph. Thereby, a complex phase mixture of 4H, 6H, and α -phase together with potential MAI-PbI₂-based solvent intermediates is established, which is converted into pure perovskite phase by thermal annealing.²⁹²

The crystallization pathway can be manipulated by adding further cations such as cesium. Its presence has shown to promote formation of the α -phase.^{292–294} Addition of rubidium is instead considered to suppress formation of solvate phases and favor direct formation of the 6H phase.²⁹³ Thus, addition of both rubidium and cesium cations simultaneously suppresses both solvated and hexagonal phases and promotes cubic phase formation in a synergistic effect.

The time window for further processing or quenching steps can be manipulated by compositional tuning as well, to kinetically stabilize the disordered precursor phase and delay the formation of the crystalline intermediate since demixing and growth of multiple distinct phases is required.^{295,296} However, the simultaneous growth of multiple compositionally different phases can lead to compositional inhomogeneities in the film, which might be potential sites of degradation or nuclei for phase segregation.

Growth of Layered Structures Similarly to the 3D perovskite structures, layered perovskite structures are formed in several stages. Notably, the crystallization pathway is likely to be strongly influenced by the type of spacer cation and thus the type of structure formed as well as the composition, especially the intended layer number n . In the following, general principles of layered structure formation are discussed briefly, which apply to simple molecular spacer cations such as aliphatic or aromatic amines. A general understanding of the formation and growth of layered structures is beneficial for understanding the results of the various layered architectures in Chapter 11.

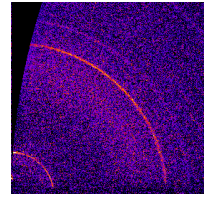
Upon deposition of a 2D perovskite precursor solution, a disordered precursor gel initially forms an oriented 3D-like structure, which then crystallizes into a layered structure.^{237,297} The formation of layered intermediate structures can be beneficial in this case since those can template and control the crystal orientation.¹⁰⁴ Generally, layered structures exhibit a high degree of crystallinity and an inherent orientational order due to their formation via self-assembly, which in most cases renders thermal annealing unnecessary.⁷⁵



4.2. CRYSTALLIZATION OF PEROVSKITE PHASE

The before-mentioned phase distribution in higher n compositions with smaller n phases close to the substrate and larger n and 3D phases located in proximity to the film surface can be adjusted by manipulating the crystallization kinetics.²⁶⁹ It is assumed to arise due to a concentration gradient during crystallization, enabling slow growth of oriented small- n layered phases close to the substrate simultaneous with faster supersaturation at the surface of the drying film. This leads to growth of 3D and higher n phases from the liquid-air interface.²⁹⁷ Since evaporation rates and the formation of possible intermediates, which both ultimately define crystal quality and orientational order, are determined by the solvent mixture, selecting the types and ratios of the employed solvents can be applied to tune the layer thickness distribution and orientational order.^{104,298}

Lastly, the formation of 2D/3D architectures, where a solution of the halide salt of a spacer cation is deposited onto a pre-fabricated perovskite thin film, is achieved by sequential incorporation of the spacer cations into the 3D lattice. For aromatic spacers, this can be supported by phenyl ring stacking. The introduction of spacer cations is supposed to take place via dimensional reduction from the 3D structure over higher n layered structures subsequently lowering n to form the layered structure.²⁹⁹



4.3 Device Fabrication

To create a functioning photovoltaic, or any other, device based on a perovskite material, many more components are required besides the perovskite thin film.⁶ These components include charge extraction layers, electrodes, encapsulations and possible further connection layers. The commonly applied architecture is shown schematically in Figure 4.3, where the perovskite layer is sandwiched between a hole transport layer (HTL) and an electron transport layer (ETL) to enable selective out-coupling of charges and thus facilitate charge separation to achieve a high open-circuit potential and reduce recombination.^{300–302} These charge transport layers can be constructed of organic³⁰⁰ or inorganic materials,^{302–305} which require careful selection to match the energy levels of the absorber material.^{300,302,304,305} Common materials include TiO_2 ,³⁰⁴ NiO_x or ZnO ,^{303,305} as well as the most widespread organic hole transport material spiro-OMeTAD (2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene).^{306,307} Possible alternatives include various small organic molecules or polymers.^{306,308} The selection of suitable charge transport layers affects operational device stability as well,^{303,309,310} which is described further below.

The stack of perovskite absorber layer and charge transport layers is, in turn, sandwiched by thin layered electrodes. For the top-side electrode, this is frequently comprised by a transparent conductive oxide such as indium tin oxide (ITO) or fluorine-doped tin oxide

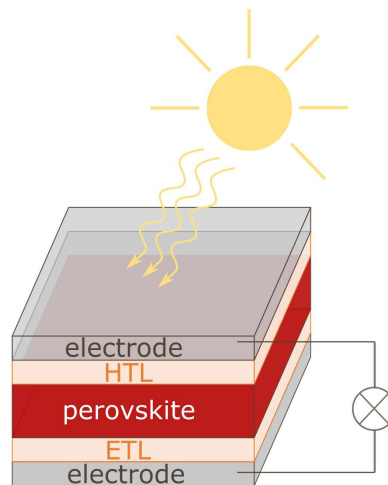
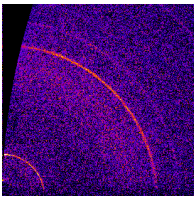


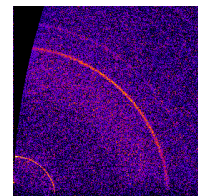
Figure 4.3: Schematic representation of the architecture of a perovskite solar cell. HTL = hole transport layer, ETL = electron transport layer.



(FTO), which doubles in function as a substrate for thin film deposition of the stack components. The back-side electrode is generally a metal electrode of a vapor deposited gold layer, while alternatives such as conducting polymers are under investigation as well.³⁰⁶ Similar considerations as for the charge extraction layers apply in selecting the electrode materials in terms of optimization of performance and stability.

Thus, fabrication of a photovoltaic device not only requires deposition of a perovskite thin film, but several layers of different materials. Suitable deposition methods have to be devised in order to not damage the underlying layers, but still allowing optimal morphology control.

Even more complexity is introduced when fabricating tandem solar cells, where for example a perovskite absorber is applied as a top cell on a silicon back cell. These can be mechanically stacked (4-terminal) or monolithically integrated (2-terminal) to reach combined power conversion efficiencies of over 30 %.²⁸ Since the major current losses in such stacked devices occur due to processes like reflection or parasitic absorption,³¹¹ the materials, thicknesses and geometries require careful selection to avoid creation of light-trapping architectures. In monolithic constructions, the interconnect between the two sub-cells plays a vital role, which is the subject of Section 13, based on publication [X].



Chapter 5

Challenges

Although hybrid halide perovskites are a promising material for the solar energy of the future, there are serious challenges that require addressing until perovskite solar cells can hit the mainstream market. These include toxicity issues of the materials themselves,^{312, 313} containing lead compounds³¹⁴ as well as the application of harmful solvents in production. In both cases a less toxic alternative is yet to be established. Large scale production of perovskite solar panels is a challenge in itself since most record-breaking devices have only been fabricated on laboratory scale with a few centimeters in size and yet require upscaling.²⁷⁸ Lastly, the long term stability of these devices is another parameter which still requires drastic improvement in order to create competitive perovskite photovoltaics.³¹⁵ While these concerns are beyond the scope of this work, they require to be mentioned since they pose drawbacks on the commercial breakthrough and therefore can map out areas where research expansion is necessitated.

5.1 Environmental Impact

Despite most vocalized concerns about the hybrid perovskite materials concerning the usage of lead, which is discussed below, the other components including solvents and processing agents require consideration as well when assessing the environmental impact and toxicity of perovskite photovoltaics.

Lead is well-known for its neurotoxicity, however methylammonium has likewise shown to be toxic.³¹³ The overall environmental impact has been claimed to be even larger for the methylammonium halides than for the lead halides when considering the whole life cycle, while the largest impact is created during fabrication.³¹² Considering finished perovskite photovoltaic devices, special attention is required as well since the structural integrity has

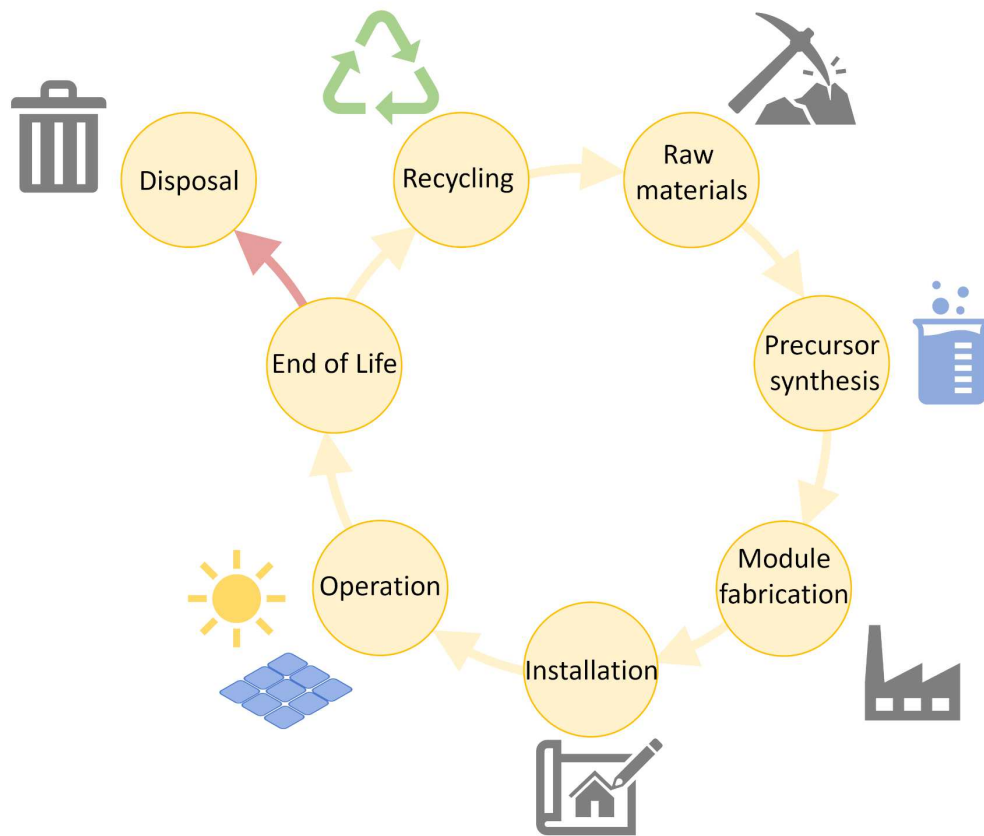
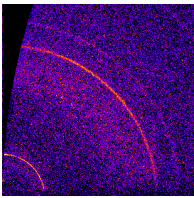
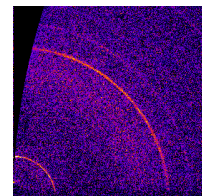


Figure 5.1: Schematic depiction of a life cycle of a (perovskite) solar cell. In assessing environmental impact of a device, all stages of the life cycle have to be taken into account.

to always be ensured to prevent leakage of components, requiring for example encapsulation of devices or special precautions to catch eventual leakage products. As with all solar cells, fire is a serious hazard, which for perovskite materials includes the spread of toxic fumes.^{314,316}

However, considering the environmental impact of the whole life cycle, including cumulative energy demand, effects on climate change and human toxicity, the impacts of the common perovskite components (MAI, FAI, CsI, PbI_2) are similar to each other and ~ 1000 times smaller than that of glass, so the total lead emissions per kWh of produced electricity can be even lower than for the current grid electricity of western countries.³¹⁷ Precautions still have to be taken to design the production and usage of perovskite materials as safe and sustainable as possible. The other layers of photovoltaic devices apart from the perovskite require close monitoring of their environmental impact as well, which might be even higher than that of the perovskite itself.³¹⁷



CHAPTER 5. CHALLENGES

Perovskite-based photovoltaic devices are usually comprised of many materials, each of which exerts its own environmental impact. A full life cycle analysis (see Figure 5.1) of a perovskite solar cell includes the resources, energy usage, byproducts, costs and emissions of all components including extraction and contact layers.³¹⁸ Thus, the focus of optimization and finding sustainable alternatives should include all possible components of perovskite-based solar cells.

Since the full life cycle of a device includes disposal or re-utilization of the components, solar cell recycling is a pressing research demand as well. On laboratory scale, disassembly and recycling of the different materials has produced promising results.^{319,320} As with device production, however, it yet has to face the challenges of upscaling and industrialization, as described below.

Lead Toxicity As mentioned above, the toxicity of lead is one of the most recognized dangers of hybrid perovskite materials and great efforts have been exerted to develop alternatives (Figure 5.2). Human uptake of lead can occur gastrointestinally, respiratory and dermally. Damage in the body is done through mimicry of essential elements and long-term accumulation.³¹⁴

As possible candidates for replacing lead, several elements such as tin or germanium as well as cobalt, strontium or various rare earth metals have been proposed.^{142,321–324} Of these, only tin and germanium are able to form the traditional perovskite structure, while thin films of MASnI_3 have been found to exhibit a cubic α -phase even at room temperature.³²⁵

However, although lead compounds can be stable in air on a time scale of several months,³⁵ tin-based materials decompose quickly due to oxidization of Sn^{II} to Sn^{IV} .^{35,326} Furthermore, tin halides are highly toxic materials as well, and thus are likely not a suitable replacement for lead compounds for the purpose of toxicity reduction.³²⁷

Many further candidates on the list for replacing lead in perovskite materials have likewise experienced serious drawbacks such as difficulty of solution processing, unsuitable band gaps or structural instabilities.³²⁸

An alternative approach are double perovskites, where lead is replaced not by a single type of ion, but two types of ions in a 1:1 mixture, which can be a larger and smaller species or a mono and trivalent species, arranged alternately to replace the bivalent lead cation.^{329,330} For these materials, issues such as structural stability and precursor availability require consideration as well, while the toxicity of these double perovskite materials is mostly unexplored.

Thus, while there are promising concepts, direct replacement of lead would impose major

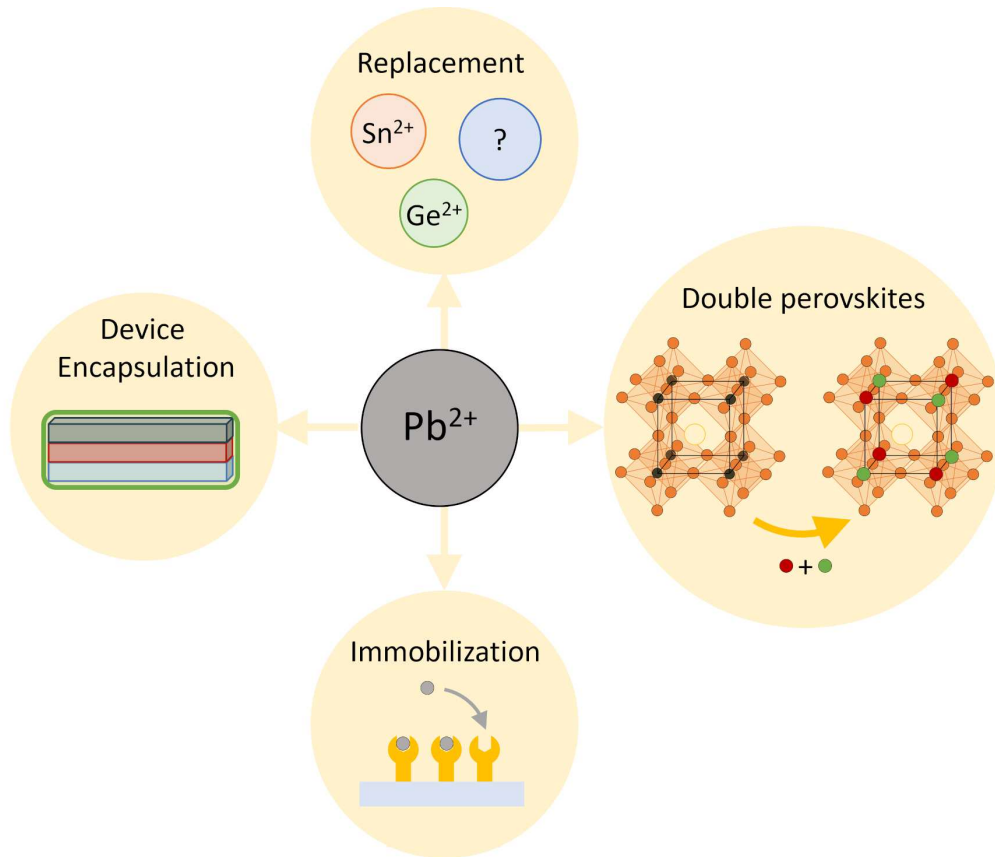
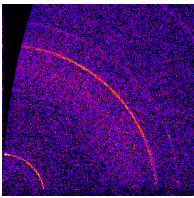
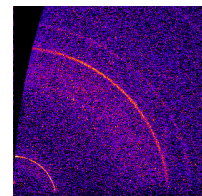


Figure 5.2: Strategies investigated in order to overcome toxicity issues in present perovskite solar cells induced by the application of lead cations.

challenges on the development of perovskite photovoltaics. Lead-based materials are still leading the performance field by a large margin, thus further possibilities such as lead fixation and lead capture mechanisms in case of device fault are worth taking into consideration.^{316,318} One possible route for lead fixation is presented in Section 9.2.

Importantly, further materials and process steps for photovoltaic devices require consideration of their toxicity potential as well and so do the ones for conventional solar cells.^{315,331} In any case, for a technology attempting to produce environmentally friendly electricity, any additional toxicity and pollution should be avoided, which still requires research and optimization.

Toxic Solvents Besides the materials which are contained in the final device, consumables and auxiliary materials applied during fabrication should be considered in a technology's environmental impact as well. Although possible energy consumption could be, by orders of magnitude, lower for perovskite-based solar cells than the commercial

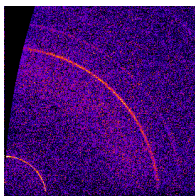


CHAPTER 5. CHALLENGES

silicon cells due to the ease of solution-based fabrication, handling of perovskite solutions creates its own concerns. The usage of toxic solvents in perovskite layer fabrication can be a hazard to manufacturers and researching scientists. Commonly employed solvents include dimethylsulfoxide (DMSO), which possesses skin penetrating abilities,³³² dimethylformamide (DMF), which is harmful upon inhalation or skin contact,³³³ and N-methyl-2-pyrrolidone (NMP), which can irritate skin and respiratory system,³³⁴ while the latter two are even considered to be reprotoxic.^{333,334} The miscibility of these solvents with water only multiplies their hazard. Solubilization of perovskite precursors increases the bioavailability, therefore perovskite precursor solutions are dangerous liquids that require handling with well advised care.³¹⁴

Less harmful solvents remain critically under-explored, although promising results have been achieved for example with a mixture of γ -butyrolactone (GBL), ethanol and acetic acid.³³⁵

Even more concerning is the usage of antisolvents in most lab-based fabrication methods, which are applied in even higher amounts than the actual solvents for the precursors and are often similarly toxic materials such as the widespread chlorobenzene.^{336,337} These require replacement by less toxic alternatives,^{338,339} or, for the sake of industrialization and implementation into production lines, complete omission by the utilization of alternative quenching techniques such as nitrogen-assisted drying.^{280,340}



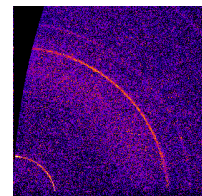
5.2 Upscaling

For the commercialization of perovskite-based devices such as solar cells, processes and facilities for mass production are yet to be established. Many lab-based techniques like the popular spin-coating are not applicable for large scale production of solar panels with appropriate sizes and create additional issues such as high solution waste during fabrication.²⁷² In general, most research is done on single centimeter-sized samples, while larger size specimen are lacking behind the laboratory scale thin films in terms of performance and consistency.²⁷⁸

Thus, deposition methods have to be established, which can be implemented on a larger scale, ideally in roll-to-roll processes, but still allow sufficient control over the deposition process and the resulting layer morphology to enable uniform deposition of perovskite thin films. Similar considerations likewise apply to the deposition of further components of a photovoltaic device such as charge transport layers, electrode materials and coatings, which have to be scaled accordingly in compatible processes.

Commonly applied quenching techniques, especially antisolvent application, are likely unsuited for large scale roll-to-roll fabrication as well. Therefore, antisolvent-free deposition methods should be favored.

Vapor assisted or vacuum-based processes, even though they offer benefits such as high purity, stoichiometry control and are free of solvents that could harm underlying layers, require complex setups and energy-consuming vacuum maintenance and heating of evaporation cells. This would significantly increase energy expenditure during fabrication, impeding energy-efficient production, which is seen as one of the main benefits of perovskite photovoltaics.



5.3 Stability

Solar modules usually are devices built and installed for long-term usage, often in harsh environments, i.e. outdoors on rooftops or fields. Thus, they have to withstand various weather conditions and seasons while staying functional over long periods of time. This is a major issue for perovskite-based solar modules, which have been struggling to reach sufficient operational stability.³⁴¹

Hybrid organic-inorganic perovskite materials possess an intrinsic instability, which highly depends on the material composition.³⁴² Water, oxygen, heat and even light are environmental factors that can induce degradation of especially methylammonium-based materials.^{138, 159, 342, 343}

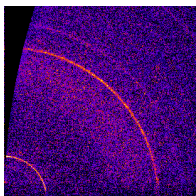
Due to this intrinsic thermal instability, significant decomposition is already observed at 85 °C,¹³⁸ which is likely to be reached during operation in full sunlight, leading to an irreversible loss of the components, which is lethal for a device.^{160, 344} The presence of oxygen or water have been found to accelerate the thermal degradation of MAPbI₃ materials further.¹³⁹

Water on its own is one of the major threats towards the integrity of MAPbI₃ perovskite materials, quickly and irreversibly decomposing it into PbI₂ and aqueous methylammonium iodide.^{345, 346} Exposure to oxygen and water vapor at the same time has shown to lead to further and complete degradation of all components.^{159, 346}

Oxygen is thus, after water, the second major source of degradation compromising the integrity of perovskite and especially MAPbI₃ materials.³⁴³

The structural stability of perovskite layers in photovoltaic devices is critically linked to their operational stability. Degradation of absorber materials inevitably leads to simultaneous demise of performance. Thus, great efforts have been undertaken to stabilize perovskite materials against degradation.²⁷⁸ Compositional engineering, which is discussed mainly in Chapter 9, has been successfully applied to increase intrinsic stability of the material, while formation of low-dimensional perovskite structures including slightly larger hydrophobic molecular cations are especially promising for humidity resistance.²³³ These types of structures are discussed in Chapter 11.

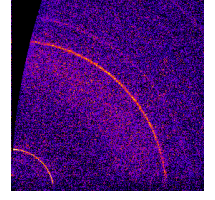
Sealing of devices prohibits exposure to ambient air and moisture, which is crucial to preserve material integrity. Thus, device encapsulation is not only important for preventing leakage of materials into the environment as described above on the example of lead, but plays a vital role in retaining materials stable and operational.³⁴⁷ Additionally, the choice of device components, such as charge transport layers or electrodes can dramatically affect the stability of the perovskite active layer.^{278, 303, 309}



5.3. STABILITY

All of the potential environmental advantages of perovskite solar cells, such as possibly less energy and resource usage than established solar modules can only unfold their benefits if the modules possess comparable lifetime under real-world operation.³¹⁵

II EXPERIMENTAL METHODS



Chapter 6

X-Rays and Their Interaction with Matter

Discovered in 1895 by Wilhelm Conrad Röntgen,³⁴⁸ X-Rays have evolved into a powerful and versatile tool not only for crystallographers or medical practitioners but for various further applications in science and technology. For unraveling the structure of a large range of materials, X-rays are the means of choice. Due to their wavelength range coinciding with the sizes of atomic and molecular structures, these can be investigated by different X-ray techniques, a selection of which is described in detail in the following sections. This chapter focuses on the fundamental principles of X-ray scattering and diffraction, mainly based on reference [349] while Chapter 7 introduces different X-ray based techniques.

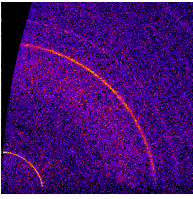
X-rays are electromagnetic waves with wavelengths in the length scale of Å(10^{-10} m). Therefore, they can be described as a propagating wave with a wavelength λ . Alternatively, the wavenumber $k = \frac{2\pi}{\lambda}$ or frequency $\omega = 2\pi\frac{c}{\lambda}$, with c the speed of light in vacuum, can be used. In a classical description, the propagating electromagnetic wave can be characterized by a spatially and temporally variable electric field

$$\vec{E}(\vec{r}, t) = \vec{E}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad (6.1)$$

Here, the direction of the wave vector $\vec{k}$ points along the direction of propagation, whereas $\vec{r}$ and t are spatial and temporal variables, respectively.

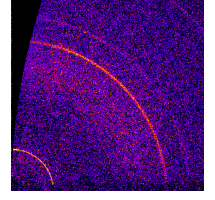
In a quantum mechanical picture, however, X-rays can be described as photons, similar to visible light. These quantized quasi-particles can then be characterized by their energy $\hbar\omega$ and their momentum $\hbar\vec{k}$.

Consequently, the interaction of X-rays and matter can be described from two different



perspectives: First, the macroscopic level, for which materials are treated as a continuum with a certain refractive index and an interface to the surrounding medium. At these interfaces phenomena such as refraction and reflection occur. Second, on the atomic level, phenomena such as absorption and scattering as well as diffraction from crystals or in general ordered systems can be explained.

The following two sections provide a short overview of the important processes that can be explained from either perspective, including definitions of the terminology.



6.1 Refraction and Reflection

Refraction is the change of direction which an electromagnetic wave experiences when passing from one medium to another as depicted in Figure 6.1. If the wavefront impinging on an interface returns into the medium it originated from, the process is called reflection. For specular reflection, the angle of reflection is equal to the incident angle.

To describe the propagation of X-rays in matter, similar to visible light, the complex refractive index (n) of a homogeneous medium

$$n = 1 - \delta + i\beta \quad (6.2)$$

can be divided into real and imaginary parts. The real part δ describes dispersion, i.e. the dependence of phase velocity on frequency and can be written as

$$\delta = \frac{2\pi}{k^2} \rho_e r_0 \quad (6.3)$$

with ρ_e the electron density of the material, r_0 the classical electron radius and k the wavenumber as defined above. The imaginary part β describes absorption and is given

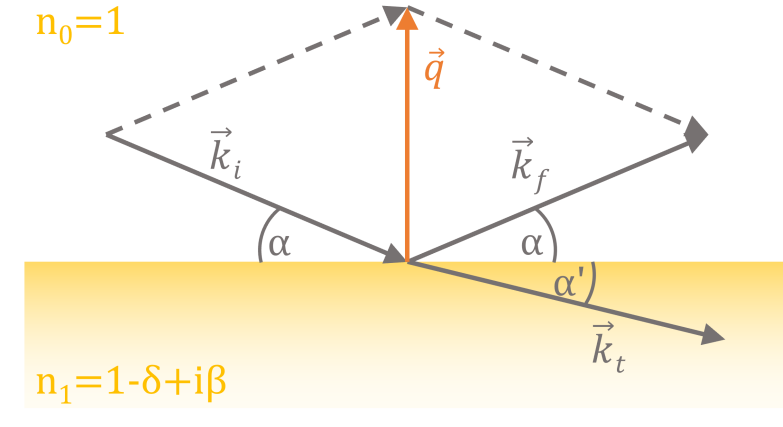
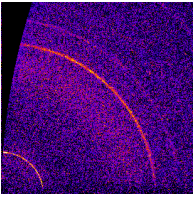


Figure 6.1: Schematic representation of X-rays being reflected and refracted at an interface. $\vec{k}_i$ and $\vec{k}_f$ denote the wave vectors of the incident and scattered beam, respectively, while $\vec{k}_t$ indicates the transmitted beam. α is the incidence angle which is equal to the reflection angle. α' is the angle of the transmitted beam after refraction. The refractive indices of the surrounding medium and the thin film are indicated by n_0 and n_1 , respectively. A visual definition of the scattering vector $\vec{q} = \vec{k}_f - \vec{k}_i$ is provided, which is detailed below.



6.1. REFRACTION AND REFLECTION

by

$$\beta = \frac{1}{2k}\mu \quad (6.4)$$

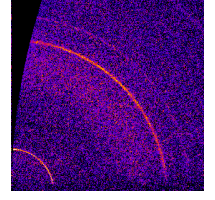
including the absorption coefficient μ , whose origin is described later on.

The refractive index can be applied to relate the incident angle with which radiation hits an interface between two media to the angle of transmission in the second medium. Snell's law specifies their relation in the following way:

$$n_0 \cos(\alpha) = n_1 \cos(\alpha') \quad (6.5)$$

with $n_{0,1}$ the refractive indices of the interfacing media respectively, and the incident and transmission angles α and α' in the respective media. Since δ is a positive value, the refractive index for X-rays in most media is below unity. As can be deduced from equation 6.5, this leads to a certain angle of incidence, where the transmission angle $\alpha' = 0$. This angle of incidence is called the critical angle α_c . The critical angle can be approximated as $\alpha_c = \sqrt{2\delta}$. For incidence angles $\alpha < \alpha_c$, total external reflection is observed, with exponentially small transmission of radiation through the sample.

Furthermore, the refractive indices together with the incident angle can be applied to calculate the so-called Fresnel-coefficients, which describe reflection and transmission at an interface.



6.2 Absorption and Scattering

Considering the interactions between electromagnetic radiation and a material on the atomic level, the incoming electromagnetic waves induce oscillating dipoles in the electrons of the atoms making up the material. These in turn re-emit new electromagnetic waves which sum up to an internal displacement field

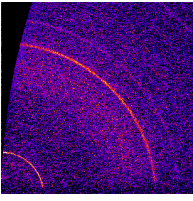
$$\vec{D} = \tilde{\varepsilon} \vec{E} \quad (6.6)$$

The relation between the external field $\vec{E}$ and the response of the material is determined by its complex dielectric function $\tilde{\varepsilon} = \varepsilon_0 \varepsilon_r$, which is a material specific property. Since the electrons in a material can not follow the external stimulus instantaneously, a phase shift between the external and internal field results, therefore the dielectric function is complex-valued. Obeying the principles of causality, the real and imaginary part of the dielectric function, ε' and ε'' , are Kramers-Kronig consistent,³⁵⁰ which allows the possibility to obtain one from the other via the Kramers-Kronig relation. To calculate the dielectric function of a material, in first approximation, the atoms can be treated as driven harmonic oscillators, although for a more in-depth calculation, quantum mechanics is required. Dielectric function $\tilde{\varepsilon}$ and the refractive index n introduced above are linked via $n \propto \sqrt{\tilde{\varepsilon}}$. In most cases, radiation is re-emitted from these oscillators with the same wavelength as the incoming radiation. This process is called elastic scattering and is solely considered here. The process of inelastic scattering, in which there is an energy exchange between the radiation and the scattering particle, is not considered further here.

The scattered intensity from a given atom is determined by its number and density of electrons and can be represented by the atomic form factor f , which is discussed further in Section 7.4. The magnitude of the atomic form factor depends on the scattering angle θ (i.e. the scattering vector $\vec{q}$) as well, such that it reaches a maximum in the forward direction ($q = 0$) and the scattering strength decreases with increasing q . Atomic form factors can be calculated from the electron density $\rho(r)$ around an atom by

$$f(q) = \int \rho(r) e^{i\vec{q}\cdot\vec{r}} d\vec{r} \quad (6.7)$$

where r is the distance from the atomic center, while their tabulated values can be found in reference [351].



6.3 X-Ray Diffraction

This section covers the basic principles of X-ray diffraction, mainly following references [349], [352] and [353]. Based on the scattering of X-rays as described in the previous section, diffraction occurs as a collective scattering phenomenon from ordered structures, leading to distinct and predictable interference patterns. In a surface scattering experiment from a thin film, the scattered intensity is recorded as a function of the scattering angle which is defined in Figure 6.2 (a). Intensity maxima are observed when constructive interference occurs, which produces diffraction peaks, as described by Bragg's law:

$$n\lambda = 2d \sin \theta \quad (6.8)$$

where λ is the X-ray wavelength, d is the associated layer periodicity, θ is the diffraction angle and n is an integer giving the diffraction order, as depicted in Figure 6.2 (a). Thus, the positions of the Bragg peaks directly relate to the periodicities within a crystal structure. Strictly speaking, Bragg's law only applies for symmetrical diffraction from a lattice plane, where incident and scattered beam possess the same angle θ respective to the surface normal.

Generally, the magnitude of the scattering vector $\vec{q}$, which is given by the wave vectors of the incident ($\vec{k}_i$) and scattered ($\vec{k}_f$) beam via

$$\vec{q} = \vec{k}_f - \vec{k}_i \quad (6.9)$$

can be calculated from the scattering angle via

$$q = \frac{4\pi}{\lambda} \sin(\theta) \quad (6.10)$$

using the wavelength λ of the X-rays.

As an alternative to the Bragg condition introduced above and in a more general way, the Laue condition can be used to explain diffraction by a crystal, describing the same phenomena by an alternative formalism, which is depicted in Figure 6.2 (b). A crystal is described by its crystal lattice, assuming identical scattering objects (i.e. atoms, ions or molecules) on each lattice position. The Laue condition is fulfilled when the scattering vector $\vec{q}$ coincides with a reciprocal lattice vector $\vec{G}$, while the reciprocal lattice is defined in wave vector space as a Fourier transform of the real-space lattice. In this case, constructive interference occurs and a diffraction signal is observed, which can then be ascribed to the diffracting plane in real space (h, k, l) , which is perpendicular to the re-

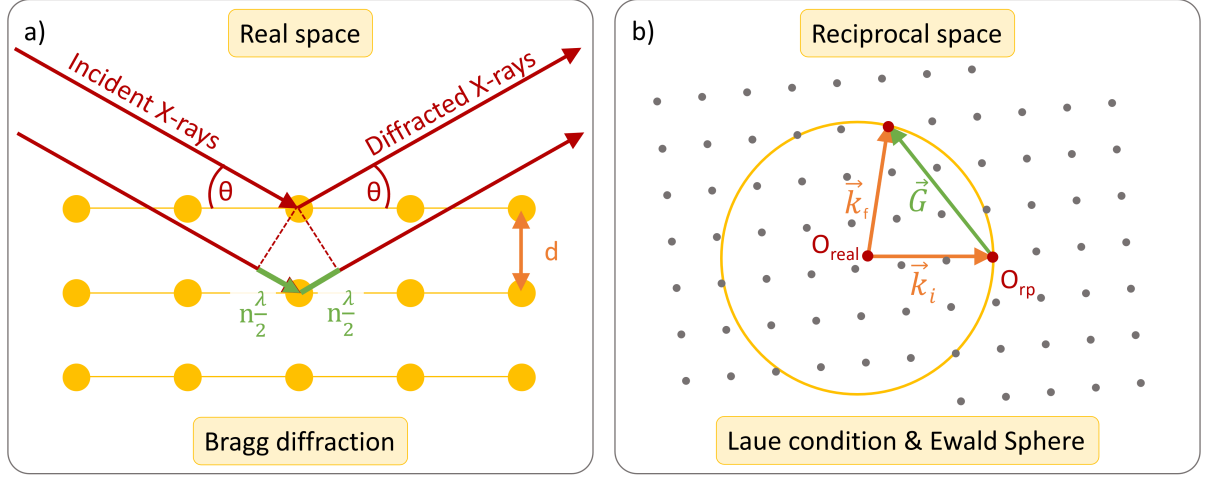
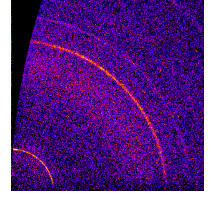


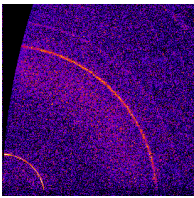
Figure 6.2: Schematic depiction of diffraction. (a) Bragg diffraction from lattice planes represented in real space. A symmetrical path difference leads to a total path difference of $n\lambda$ between the beam paths, with the X-ray wavelength λ and n an integer, leading to constructive interference. d is the layer periodicity and θ the diffraction angle as described in Equation 6.8. (b) Reciprocal space representation with Ewald sphere construction in two dimensions to visualize the Laue condition as described in the text. O_{real} and O_{rp} represent real and reciprocal space origins of scattering, while $\vec{k}_i$ and $\vec{k}_f$ are wave vectors of incoming and scattered beam, respectively. $\vec{G}$ indicates a lattice vector of the reciprocal lattice.

spective reciprocal lattice vector. An Ewald sphere is often employed to visualize the Laue condition. In short, a sphere is defined in reciprocal space such that its real space origin is at the point of diffraction, while the radius of the sphere is equal to the magnitude of the incident wave vector k_i , such that the origin of diffraction in reciprocal space lies on the surface of the sphere. For any lattice point that the Ewald sphere intersects, the precondition for elastic scattering, $k_i = k_f$ holds for the magnitudes of the wave vectors, while simultaneously the Laue condition of $\vec{k}_i - \vec{k}_f = \vec{G}$ is fulfilled and diffraction can be observed.

While the symmetry and periodicities of the crystal lattice thus determine the positions of the diffraction signals, their intensity is determined by the types and positions of atoms within the unit cell. It is described by the structure factor

$$F = \sum_n f_n(\vec{q}) e^{i\vec{q}\vec{R}_n} \quad (6.11)$$

where the sum is executed over all atoms within the unit cell and R_n is their position within the unit cell.



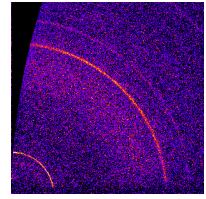
6.3. X-RAY DIFFRACTION

The final diffracted intensity (I) is proportional to the square of the structure factor, $I \propto |F|^2$. For the final signal shape, factors such as thermal fluctuations, coherent domain size and mosaicity have to be taken into account as well as the type of sample, i.e. powder, single crystal or layered structure, as is described in the next section. While thermal fluctuations can be accounted for by the Debye-Waller-factor, a small coherent domain size leads to peak broadening as described by the Scherrer Equation³⁵⁴

$$L = \frac{K \cdot \lambda}{\Delta(2\theta) \cdot \cos \theta_0} \quad (6.12)$$

which applies for crystal sizes below ~ 100 nm and includes the crystallite size L , X-ray wavelength λ , the Scherrer form factor K , which in general cases is close to 1, as well as the Bragg angle θ_0 and the width of the diffraction signal in angular space, $\Delta(2\theta)$.

In summary, a diffraction pattern with distinct diffraction signals is effectively a representation of a Fourier transform of the electron density in real space. It is recorded in reciprocal space, while 2-dimensional diffraction patterns represent reciprocal space maps, discussed further in the next section. Thus, from the peak position and the respective (hkl) indices indicating the spatial direction of the corresponding lattice plane, real-space periodicities can be inferred. Although a simple Fourier back-transform is not possible due to the phase information being lost when measuring intensities, model calculations can serve to elucidate atomic-level structures as is further described in Section 7.4.



Chapter 7

X-ray Techniques

On the basis of the processes presented in the previous chapter, the following sections describe specialized X-ray techniques such as grazing incidence diffractometry and X-ray reflectometry and the setups used to perform these measurements. The technique of anomalous X-ray scattering and the associated opportunities and challenges are presented as well.

7.1 Grazing Incidence Wide Angle X-Ray Scattering

In grazing incidence wide angle X-ray scattering (GIWAXS), as the name suggests, X-ray scattering is performed under shallow incidence angles while recording the diffraction patterns with a two-dimensional detector covering a large range of reciprocal space. Both of these characteristics offer unique possibilities but special challenges as well, as is described within this section, based on references [349], [352] and [353].

Incidence Angle and Penetration Depth As mentioned previously, for X-rays impinging on a material, there exists a critical angle, below which total external reflection occurs. When measuring GIWAXS, the incidence angles are usually chosen close to the critical angle of the investigated thin film. This creates evanescent waves along the film surface, enhancing the scattering intensity from the surface, thus enabling a surface-sensitive measurement. Variation of the incidence angle then tunes the surface sensitivity and probing depth, enabling depth dependent structural analysis as depicted in Figure 7.1. The probing depth Λ can be calculated from the incidence angle and material specific critical angle by distinguishing three cases:

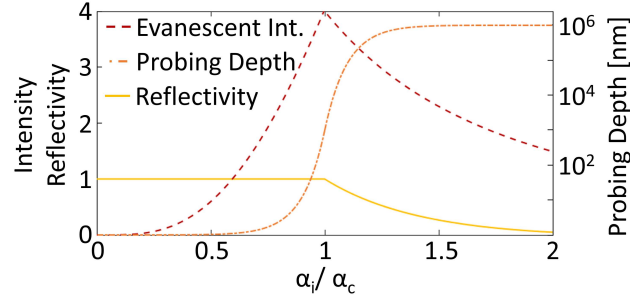
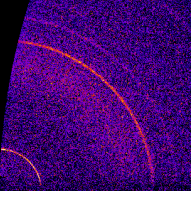


Figure 7.1: Theoretical Fresnel reflectivity, transmitted evanescent intensity and penetration depth in units of the critical angle α_c of a MAPbI_3 thin film, assuming infinite thickness. Figure adapted after [349], absorption coefficient taken from [355].

- $\alpha_i < \alpha_c$: total external reflection, probing only the very surface, $\Lambda = \frac{1}{2k\alpha_c}$
- $\alpha_i \simeq \alpha_c$: Highest sensitivity towards regions close to the sample surface, $\Lambda = \frac{1}{2k\alpha_c\sqrt{b_\mu}}$
- $\alpha_i > \alpha_c$: Probing depth depends on incidence angle, $\Lambda = \frac{\alpha_i}{\mu}$

with the wave vector magnitude of the probing X-rays k , absorption coefficient μ and the coefficient $b_\mu = \frac{2k}{(Q_c)^2}\mu$, where $Q_c = 2k\alpha_c$ is the scattering vector at the critical angle. Along with the possibility of depth dependent analysis emerge certain challenges when measuring at shallow incidence angles. Besides the premise of exact alignment and precise instrument movement, these include refraction effects which require to be corrected for during data evaluation. An increased footprint of the beam on the sample is another side effect of small incidence angles, which can generate undesired features such as double diffraction peaks.

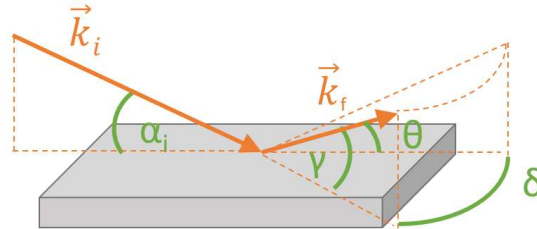
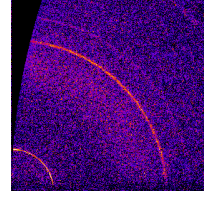


Figure 7.2: GIWAXS geometry and definition of associated angles. α_i is the incidence angle of the X-ray beam. θ denotes the angle of the scattered intensity, while δ and γ are its horizontal and vertical components, respectively. $\vec{k}_i$ and $\vec{k}_f$ indicate the wave vectors of incident and scattered X-ray beams.



Conversion of Measured Angular Data into Reciprocal Space Maps For measuring GIWAXS, usually an area detector is applied to record a large range of q -space simultaneously. The resulting data is converted from angular space into reciprocal space maps by

$$q_z = \frac{2\pi}{\lambda} (\sin \alpha_i + \sin \gamma) \quad (7.1)$$

$$q_{xy} = \frac{2\pi}{\lambda} \sqrt{(\sin \delta \cos \gamma)^2 + (\cos \gamma \cos \delta - \cos \alpha_i)^2} \quad (7.2)$$

with the X-ray wavelength λ , and the angles α_i , γ and δ defined as depicted in Figure 7.2.

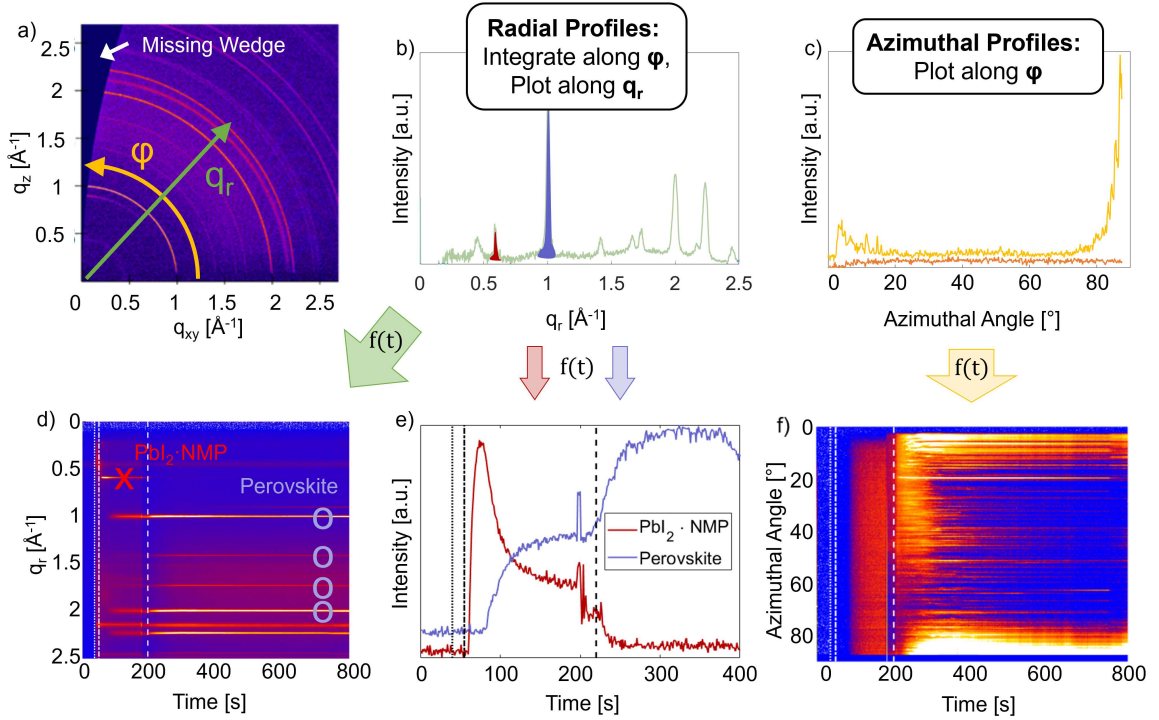
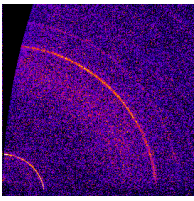


Figure 7.3: Illustration of typical analyses done on (in-situ) GIWAXS data. (a) Exemplary reciprocal space map of a MAPbI_3 thin film. (b) Azimuthally integrated radial profile, i.e. intensity as a function of $|q_r|$. Areas shaded in red and blue indicate integrated signal intensities of the $\text{PbI}_2 \cdot \text{NMP}$ and perovskite phases, respectively. (c) Intensity of the (110) perovskite diffraction signal at $q = 1 \text{\AA}^{-1}$ as a function of azimuthal angle, i.e. along the diffraction ring. (d) Radial profiles as depicted in (b) as a function of time, using a colormap of blue = low intensity to yellow/white = high intensity. Signature peaks of identified crystal phases are marked: red crosses indicate the $\text{PbI}_2 \cdot \text{NMP}$ phase, while blue circles indicate perovskite. (e) Integrated peak intensities as indicated by shaded areas in (b) as a function of time. (f) Azimuthal intensities as shown in (c) as a function of time, using a similar colormap as in (d).



The in-plane directions are summarized into one component q_{xy} , while usually in-plane isotropy is assumed. The conversion from the angular space recorded with a flat detector into q -space generates the so-called ‘missing wedge’, a wedge-shaped area along the q_z direction in which data cannot be accessed in the GIWAXS geometry (see Figure 7.3 (a)). This is due to a non-negligible q_x component for large measurement angles along q_z , creating a projection of the curved surface of the Ewald sphere onto a 2D detector.

Further correction factors have to be applied when converting data from angular space into reciprocal space. Most importantly, these include Lorentz and polarization correction.³⁵⁶ Those account for the angular dependence of the scattered intensity defined by measurement and sample geometry as well as the polarization of the probing X-rays. Additionally, several instrument related intensity corrections can be applied, including background subtraction, detector flat field and efficiency correction, dark field correction and many more.³⁵⁷

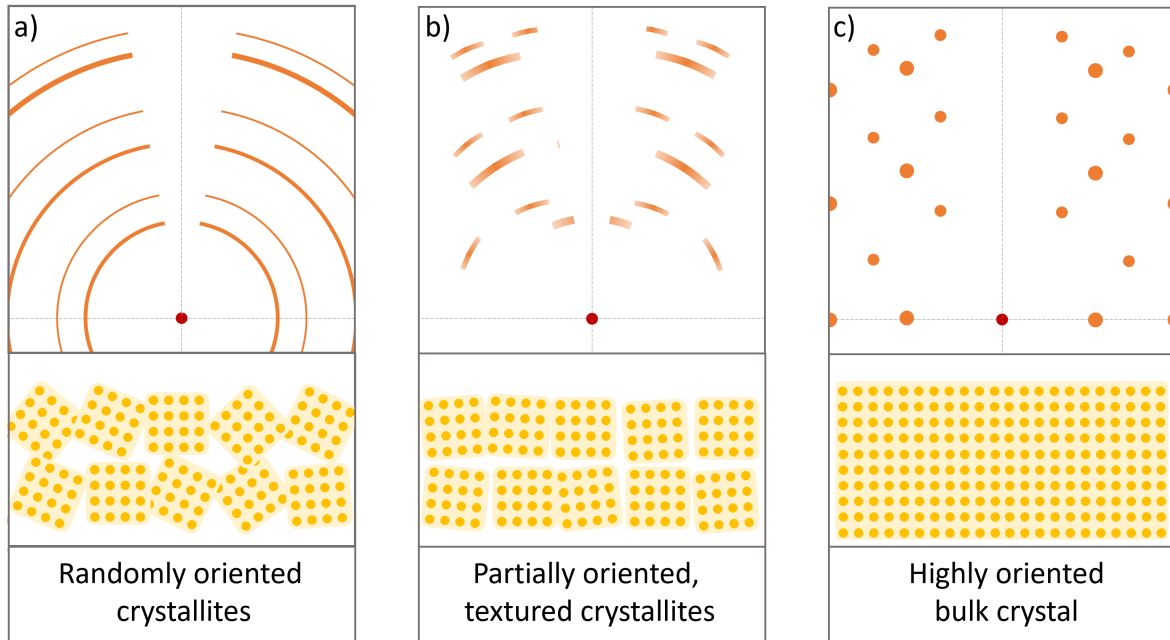
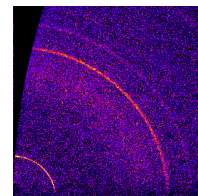
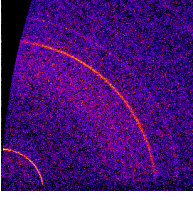


Figure 7.4: Schematic representation of selected common types of two-dimensional diffraction patterns obtained from materials with different types of order: (a) Debye-Scherrer Rings originating from randomly oriented crystallites, (b) textured material producing arc shaped diffraction features and (c) well-ordered crystalline material creating sharp diffraction spots.



Extracting Information from GIWAXS Data Measuring diffraction patterns in two dimensions renders information accessible, which can not be readily obtained by standard X-ray diffraction (XRD) analysis such as in-plane structures and texture. Figure 7.4 contains schematic depictions of measured intensities in GIWAXS experiments for exemplary cases. Analysis of diffraction signals along the azimuthal direction will thus provide information on the thin film texture. When measuring very thin films, finite crystal effects can occur, such as crystal truncation rods.

Furthermore, many standard analyses that are done with XRD data can be performed with azimuthally integrated radial profiles (see Figure 7.3) of high quality GIWAXS reciprocal space maps as well, such as line profile analysis and phase identification. For quantitative analyses, while the 2D measurement allows to include all different crystallite orientations, the presence of the missing wedge requires to be taken into account. To obtain information along the true vertical q_z axis, X-ray reflectometry as described below can serve as a complementary tool.



7.2 X-Ray Reflectometry

X-ray reflectometry (XRR) is a valuable tool especially for layered architectures with layers oriented in parallel to the substrate. It can complement GIWAXS by providing structural information along the z -axis of the thin film, i.e. along the surface normal. The details of the method, which will be briefly outlined in this section, can be found in references [349] and [352].

For an XRR measurement, which is performed employing a point detector, the angle of incidence is always equal in magnitude to the measurement angle to record only the specular reflected intensity. Thus, the complete momentum transfer q only possesses a non-zero value perpendicular to the sample surface along q_z . The reflection geometry for XRR is shown in Figure 7.5 (a).

By fitting the experimental data to a model of the reflectivity of a multi-layer system employing dynamical scattering theory and the Parrat-formalism,³⁵⁸ an electron density profile along the vertical direction of the sample can be obtained. A variety of properties of the investigated thin film sample can be obtained by an XRR measurement, as indicated in Figure 7.5 (b). These include:

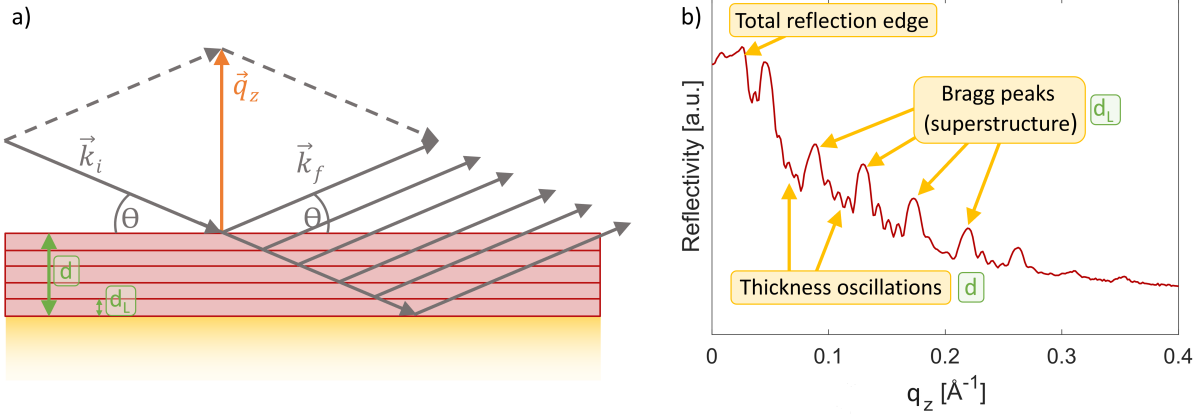
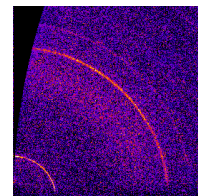


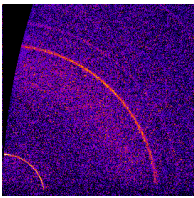
Figure 7.5: (a) X-ray reflectometry (XRR) geometry indicating thin film parameters such as the film thickness d and the layer thickness d_L of the layered superstructure. $\vec{k}_i$ and $\vec{k}_f$ indicate incoming and reflected wave vectors, respectively. $\vec{q}_z$ is the scattering vector in vertical direction and θ the Bragg angle. (b) Exemplary XRR pattern of a superstructure from alternating layers of perovskite and insulating interlayers, together with potential information obtained from an XRR pattern. Thickness oscillations are called Kiessig fringes, which occur in the low-angle reflection regime, while side fringes of the Bragg peaks are called Laue oscillations and relate to the mosaicity.



CHAPTER 7. X-RAY TECHNIQUES

- the average electron density from the position of the total reflection edge
- the film thickness from the periodicity of the thickness oscillations, i.e. Kiessig fringes, at low reflection angles
- the surface roughness from the damping of the Kiessig fringes
- the out-of-plane lattice spacing of the crystal structure or superlattice from Bragg diffraction
- the coherent domain size from the periodicity of the side fringes of the diffraction peaks, the Laue oscillations.

In this thesis, XRR is employed as a complementary tool to GIWAXS, to obtain structural information along the surface normal, which is especially crucial for layered structures such as the ones described in Chapter 11.



7.3 X-Ray Sources and Experimental Setup

This section briefly describes the X-ray sources and setups used for X-ray experiments within this thesis, including laboratory-based setups for XRR and GIWAXS as well as synchrotron beamlines. The basic principles of X-ray generation are briefly outlined for each case.

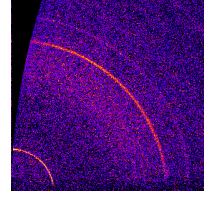
Laboratory-Based Analytics For laboratory-based X-ray reflectometry experiments, a GE XRD 3033TT diffractometer was applied, containing a copper anode with a multi-layer mirror and a germanium monochromator for $\text{CuK}_{\alpha 1}$ radiation. A NaI scintillation detector was used to record the reflected intensities. Measurements were performed in ambient atmosphere.

Laboratory-based GIWAXS was measured using a Xenocs XEUSS 2.0 laboratory beamline with a copper anode. A Pilatus 300K detector was employed to record 2-dimensional diffraction patterns. Measurements were done in an evacuated sample chamber under a pressure of ~ 0.1 bar.

In general, metal anodes are employed in laboratory-based setups as is the case here for copper anodes. Briefly, in these devices, electrons are emitted by a filament and then accelerated towards a metal anode. The electrons impacting on the metal anode create two different types of radiation: bremsstrahlung as a continuous background due to the deceleration of the electrons by the metal as well as strong lines of characteristic radiation. The latter are located at distinct energies corresponding to removal of inner shell electrons by the collision with the impinging electrons and the subsequent relaxation of outer-shell electrons, creating X-rays with element-specific energies. Usually, the K_{α} line is used due to its intensity being orders of magnitude higher than the background radiation from the bremsstrahlung, which can be filtered out by monochromators.

As a result of this creation principle of laboratory scale X-rays, the limitations to its intensity, brilliance and coherence become apparent. Furthermore, the X-ray energy is determined by the type of anode and cannot be altered. Several of these drawbacks can be alleviated by employing synchrotron radiation, as is described in the next paragraph.

Synchrotron-Based Experiments Synchrotron measurements were performed at different beamlines including DESY beamlines P08³⁵⁹ and P23,³⁶⁰ ESRF beamline ID10³⁶¹ as well as the SiXs beamline of SOLEIL.³⁶² Details on beam energies, experiment setups and parameters are listed in Table C.1 in the appendix. Measurements were performed under nitrogen atmosphere.



Real-time measurements were done at DESY beamline P08 with a temporal resolution of 0.1 s. A dedicated sample setup was employed, which is described in detail by Ekaterina Kneschaurek.³⁶³

In general, synchrotron radiation describes radiation emitted by electrons moving at relativistic speeds once they are subjected to magnetic fields forcing them into a curved path. Synchrotron facilities usually feature a storage ring where circulating electrons are stored. Radiation is produced either by the bending magnets retaining the electrons in a circular orbit or by insertion devices such as undulators or wigglers. In these devices, the electrons are subjected to spatially alternating magnetic fields to force them on oscillating paths, creating high brilliance X-rays, while small-amplitude undulators are able to create coherent radiation. A monochromator crystal is employed to adjust the X-ray energy at

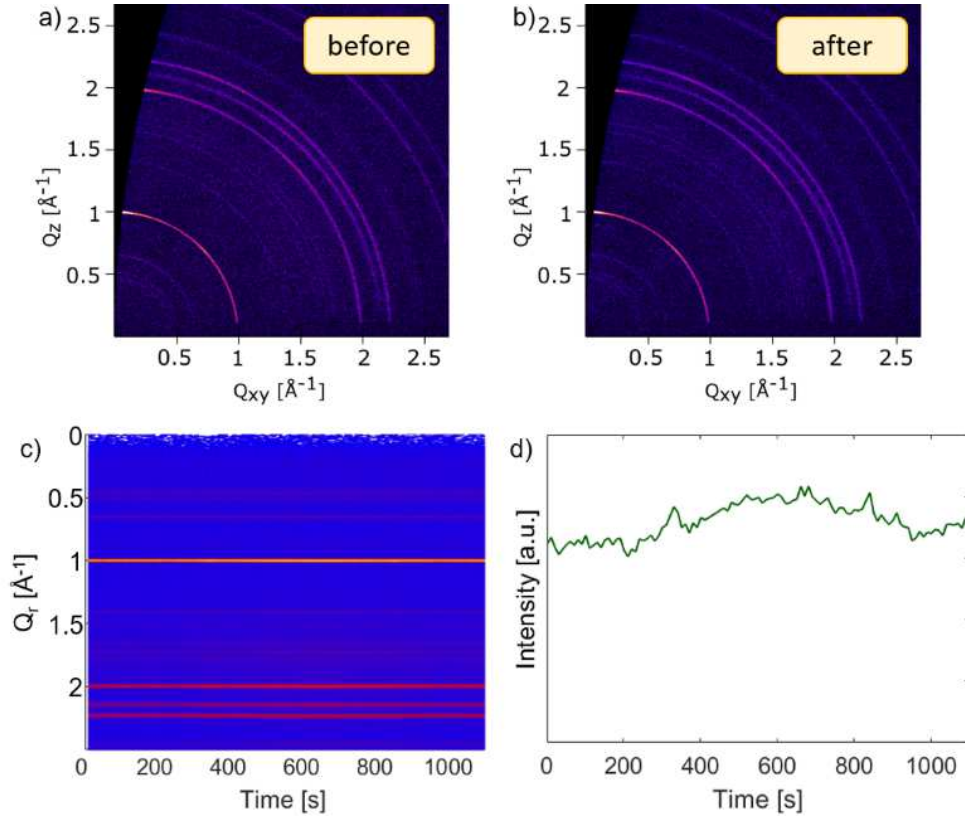
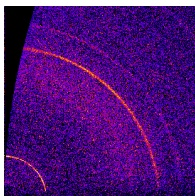


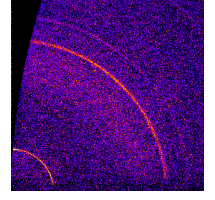
Figure 7.6: GIWAXS reciprocal space maps of a MAPbI_3 thin film (a) before and (b) after continuous exposure to X-rays for about 20 minutes. (c) Radial profiles of reciprocal space maps as a function of time. (d) Integrated intensity of the (110) perovskite diffraction signal at $q = 1 \text{ \AA}^{-1}$. Fluctuations in signal strength can be ascribed to slight variations in alignment. Similar data for MAPbBr_3 , $\text{MAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ and FAPbI_3 compositions can be found in Figures D.1–D.3 in the appendix.



the endstation to desired values for experiments, while a combination of mirrors, slits and pinholes shape and focus the X-ray beam.

Side Note on Beam Damage X-ray diffraction experiments are advertised as non-intrusive, non-destructive investigation methods. However, precautions are required to ensure that this is the case. Exposure to high doses of radiation not only would be harmful to humans, but eventually can degrade hybrid perovskite materials as well, mainly due to the presence of organic cations, which are sensitive to X-ray damage.³⁶⁴ Thus, the dose is required to be as low as reasonably achievable for good data quality, while an inert atmosphere is beneficial for alleviating radiation damage. Despite synchrotron-produced X-rays being orders of magnitude more intense than laboratory sources, they can still aid in reducing overall dose by reducing the integration time, and thus exposure time drastically. Usually, X-ray attenuators are used to adjust the X-ray intensity to a level where a non-destructive analysis is possible, which is probed via a preliminary stability test with a test sample.

This is especially important for real-time measurements, where continuous or repeated exposures are performed over a certain time frame to observe the temporal evolution of various processes. During that time, the sample should be stable against X-ray damage in order to not disturb the investigated processes. Figure 7.6 shows reciprocal space maps as well as radial profiles and integrated intensities of a MAPbI₃ perovskite thin film before, during and after continuous X-ray exposure for about 20 minutes. The measurement parameters and integration times are set to the values applied in real-time deposition experiments. As shown, the perovskite diffraction intensity remains constant over the course of the experiment, indicating that the perovskite structure is unaffected and beam damage degrading the material is not observed under these conditions.



7.4 Resonant ‘Anomalous’ Scattering and Diffraction

Resonant scattering and diffraction, frequently called ‘anomalous’ scattering, contrary to its popular name exploits the very normal behavior of X-rays at atomic absorption edges. In this section, a short introduction to the technique and opportunities of anomalous scattering is provided, which is based on reference [365]. In the last paragraphs of the section, experimental data is presented, highlighting the possibilities and challenges associated with anomalous diffraction experiments.

As introduced in Section 6.2, X-rays are generally scattered by electrons within a material that can be induced to oscillate. When the energy of the impinging X-rays matches the resonance energy of one of the inner-shell electrons, it can induce resonant excitation to a bound state, which can enhance dispersion effects near absorption edges. The atomic form factor f , as introduced in Section 6.2, which quantifies the scattering ability of a certain type of atom, becomes a complex number close to these resonance energies, i.e. absorption edges. Energy dependent correction factors have to be applied, such that the atomic form factor can be written as:

$$f(E) = f_0 + f'(E) + i f''(E) \quad (7.3)$$

where f_0 is the energy independent ‘normal’ form factor due to elastic Thomson scattering, while f' and f'' are the resonant terms, which depend on beam energy and only possess non-negligible values close to absorption edges. These are related to the macroscopic absorption coefficient μ and thus refractive index n of a material via the dispersion (δ) and absorption (β) terms

$$\delta = r_0 \frac{\lambda^2}{2\pi} N (f_0(0) + f'(\omega)) \quad (7.4)$$

$$\beta = r_0 \frac{\lambda^2}{2\pi} N f''(\omega) = \frac{\mu \lambda}{4\pi} \quad (7.5)$$

and

$$n = 1 - \delta + i\beta \quad (7.6)$$

where λ is the X-ray wavelength, r_0 the atomic radius and N the sum over all atoms/ions within the unit cell of the probed material. n is the refractive index of the material and μ the attenuation coefficient, which is experimentally accessible and can be used to determine the anomalous scattering factors f'' and f' via a Kramers-Kronig-relation.

Near an absorption edge, these undergo strong variations resulting in a sharp jump in f'' and a dip in f' , as depicted schematically in Figure 7.7. These intensity variations can

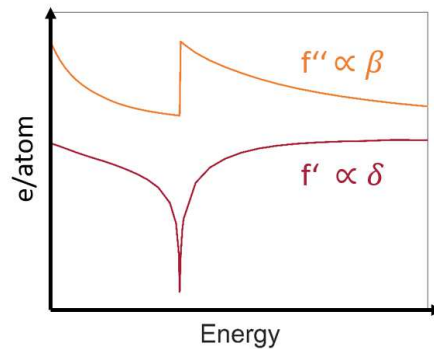
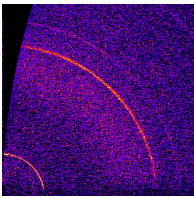
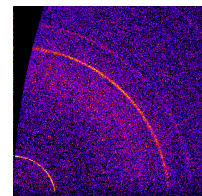


Figure 7.7: Schematic depiction of the behavior of the correction factors f' and f'' for the atomic form factor close to an absorption edge. Units in electrons per atom.

lead to phase changes of the structure factor, which is introduced in Section 6.3, resulting in variation of the diffraction intensities as a function of beam energy. Depending on the position of the resonant scattering atom within the unit cell of a crystal structure and its contributions to the different scattering planes, this creates distinct intensity behaviors for each Bragg peak, sometimes causing forbidden reflections to occur.

Anomalous Diffraction Measurements The variations in the intensity of Bragg reflections contain information on the location of the anomalous scatterers in a crystal structure, their partial structure and occupation of atomic sites. Furthermore, the dispersion effects are sensitive to the chemical state and electronic environment at the probed atom site. Altering the resonant scattering factors by varying the X-ray energy can be used to adjust the contrast between different kinds of atoms in an alloy to investigate mixing or ordering behaviors via the partial structure of one or several components.

Generally, all elements with an atomic number of $Z \geq 20$ can be used for anomalous scattering, where the absorption edges of their K or L transitions occur at energies between 4 keV and 40 keV, which are typical energies for X-ray diffraction experiments. For an anomalous diffraction experiment, several diffraction patterns are recorded at different energies close to the absorption edge of the element in question within an energy span of ~ 1 keV to track the intensity behavior of the Bragg signals over the resonance edge. To successfully track intensities over several measurements, monitoring of the incoming beam flux as well as control of systematic errors and a sufficient counting time to increase the signal-to-noise ratio is vital since the variations in signal intensity are usually much smaller than the total diffraction intensities of the Bragg peaks. A high energy resolution of about $\frac{\Delta E}{E} \sim 10^{-4}$ and energy stability of the X-ray beam are required when performing



CHAPTER 7. X-RAY TECHNIQUES

several measurements around an absorption edge as well as the detector efficiencies as a function of energy for absolute calibration. These requirements, especially quick, precise tuning of the X-ray energy are met by synchrotron sources.

The experimental data is then compared to models by simulating their expected energy dependent diffraction patterns. For these calculations, the exact values of the anomalous scattering factors are required, which enter the structure factor calculations as well as the crystallographic parameters of the material, including the atomic positions within the unit cell, geometric contributions and correction factors for polarization and Lorentz correction.³⁵⁶ Experimental parameters, such as radiation polarization, wavelength, scattering angle 2θ and the azimuth of the crystal, which can influence reflection intensities require consideration, as well as effects such as fluorescence and Raman scattering, that can create a large background intensity near absorption edges. This can be done by optimizing the setup by employing an energy sensitive detector, simultaneous background measurements or subtracting tabulated values for background effects.

Opportunities of Anomalous Scattering With its possibility to create elemental contrast, anomalous diffraction can provide answers to questions which the ‘normal’ X-ray diffraction is oblivious to. First and foremost, the presence of a certain element in a distinct crystallographic position can be determined by characteristic variations in peak intensities, which depend on the position of the element in question within the unit cell. A quantitative investigation can be performed, where the magnitude of the anomalous effect should correlate to the amount of the desired element within the crystal structure. For structures, where nonequivalent positions within a unit cell can be occupied by different types of atoms, their ordering behavior can be inferred by anomalous diffraction as has been demonstrated before on the example of kesterite types of structures³⁶⁶ or Heusler alloys.³⁶⁷ When similar crystallographic positions within a crystal structure can be occupied by different kinds of atoms, the mixing behavior is expected to influence the anomalous effect due to a diverging interference pattern between the diffracted intensities from the anomalously scattering element.

Hybrid organic-inorganic perovskite materials can contain a wide range of elements, from lighter atoms such as carbon or nitrogen up to heavy metals like lead. Thus, their absorption edge energies, which could possibly be utilized for anomalous diffraction experiments, span a wide range. For the lighter elements contained in the organic cations, these energies are below 1 keV, which is in the soft X-ray regime, requiring dedicated beamlines and experiments in vacuum to eliminate air absorption of the low-energy X-rays. The heavier elements commonly contained in perovskite structures possess absorption edges

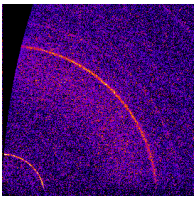


Table 7.1: Absorption edges in the X-ray regime, which can be employed for anomalous diffraction for different commonly applied elements in hybrid perovskite compositions. Values taken from reference [355].

Element	Edge type	Edge energy [keV]
Lead	L_I	15.8608
	L_{II}	15.2000
	L_{III}	13.0353
Tin	K	29.2001
Bromide	K	13.4737
Iodide	K	33.1694
Carbon	K	0.2838
Nitrogen	K	0.4016
Cesium	L_I	5.7143
Rubidium	K	15.1997

between 10 – 30 keV (Table 7.1), which is a range frequently employed for X-ray diffraction experiments and thus can be covered by many beamlines.

For inorganic perovskite materials, anomalous diffraction experiments are reported, where structural disorder,³⁶⁸ superlattices³⁶⁹ or charge ordering states³⁷⁰ have been investigated.

Challenges and Limitations of Anomalous Diffraction on Perovskites Despite the possibilities described in the previous paragraph, so far, no reports on anomalous diffraction experiments on hybrid lead halide perovskites have been published. This is surprising considering the enormous amount of research dedicated to those materials. Thus, this paragraph presents and evaluates measurements of anomalous diffraction on hybrid perovskites with different compositions to assess their usefulness, limitations and challenges.

Since lead is generally the heaviest element in hybrid perovskite compositions, it is expected to produce a distinct anomalous effect. The presence and position of the lead cation within a perovskite structure is undebated, thus measurements of anomalous diffraction on the lead L_{II} -absorption edge can serve as a proof of principle for the possibility of anomalous diffraction experiments on hybrid perovskites. Figure 7.8 shows the measured and simulated intensity variations for anomalous diffraction experiments along the lead

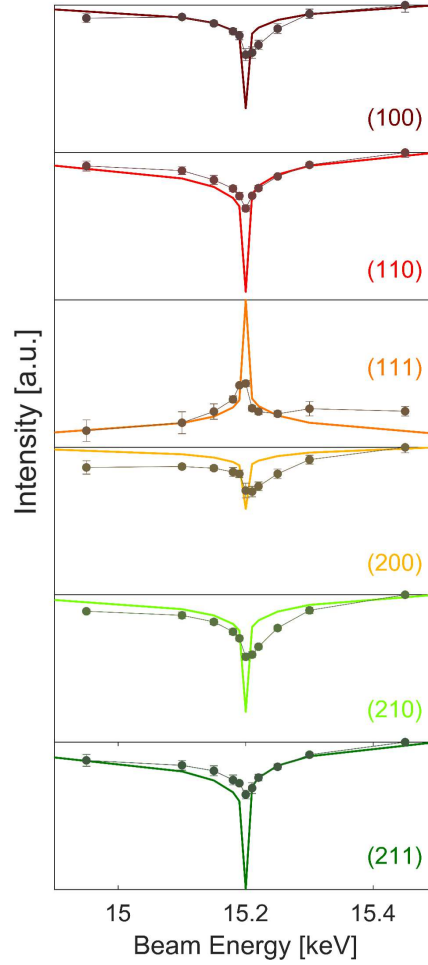
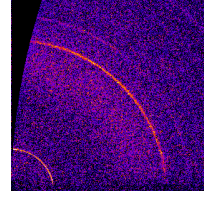


Figure 7.8: Normalized peak intensities of selected Bragg peaks as a function of beam energy around the lead L_{II} edge for a $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$ thin film. Thick solid lines: simulated data,^{89,371} darker markers with thin lines: experimental data. Colored numbers in the graphs indicate Miller indices of the respective diffraction peaks.

edge on $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$ perovskite thin films. Distinct maxima and minima are observed for the different diffraction signals, depending on the phase of the contributions of lead to the respective scattering plane. The qualitative behavior of calculated and experimentally measured peak intensities coincides, indicating the possibility to detect lead at its dedicated position in a perovskite structure.

Introduction of tin cations replacing lead in some metal cation positions within the perovskite has been proposed as a means to reduce lead toxicity in hybrid perovskite materials.³²⁴ Although this route can be considered only an interim stage in the current search for a less toxic alternative since tin possesses significant toxicity as well, as

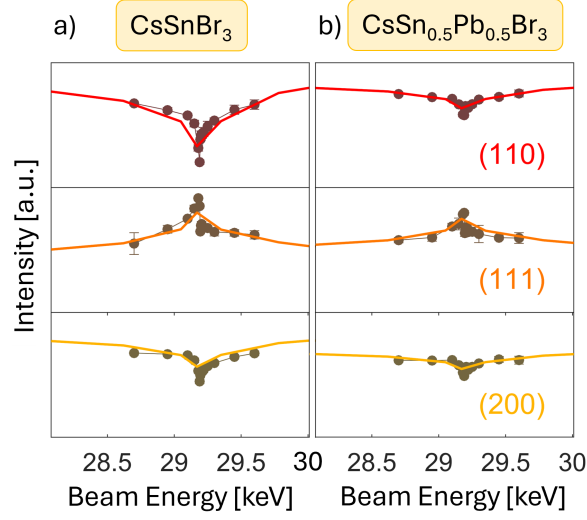
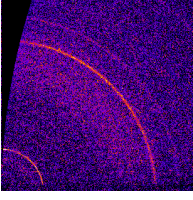
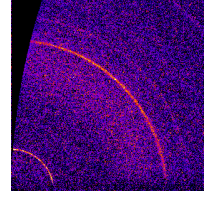


Figure 7.9: Normalized peak intensities of selected Bragg peaks as a function of beam energy around the Sn K-edge for (a) CsSnBr_3 and (b) $\text{CsSn}_{0.5}\text{Pb}_{0.5}\text{Br}_3$ thin films. Thick colored lines: simulated data,^{156,371} assuming a random mixture of tin and lead. Darker markers with thin lines: experimental data. Colored numbers in the graphs indicate Miller indices of the respective diffraction peaks. Corresponding data on the lead edge for the same samples can be found in Figure D.4.

mentioned in Section 5.1, different methods have been proposed to induce tin into existing lead halide perovskite structures. For several of them, a proof of inclusion into the desired crystallographic position is required. Thus, this purpose can be served by anomalous diffraction on the Sn K-edge. The corresponding experimental anomalous intensity variations in Figure 7.9 (b) for pure-tin CsSnBr_3 perovskite thin films correspond well to the calculated data in Figure 7.9 (a). For mixed lead-tin materials, simulations predict qualitatively similar intensity behavior to that of the pure-tin composition, but with reduced amplitudes in accordance with the reduced tin composition (Figure 7.9 (c)). This is further reflected in the experimental data in Figure 7.9 (d), which indicates successful inclusion of tin in the desired concentration in the same crystallographic position as lead. Thus, anomalous diffraction can be successfully applied to prove the presence of heavy elements in distinct crystallographic positions. An exact statement on the concentration, however, if unknown, has shown to be challenging due to experimental limitations. For determination of exact concentrations, precise values for the diffracted intensities are required. Several effects can influence and modify the measured values, including sample and setup absorption and possible re-emission, environmental scattering, detector efficiencies, input intensity variations and more. Although some of these parameters can be



accounted for by either a parallel measurement of the corresponding phenomena during the experiment or calculations, for the most precise experiment, all of these factors require exact control, which is challenging under real-world conditions since several of these effects such as absorption and re-emission mutually influence each other.

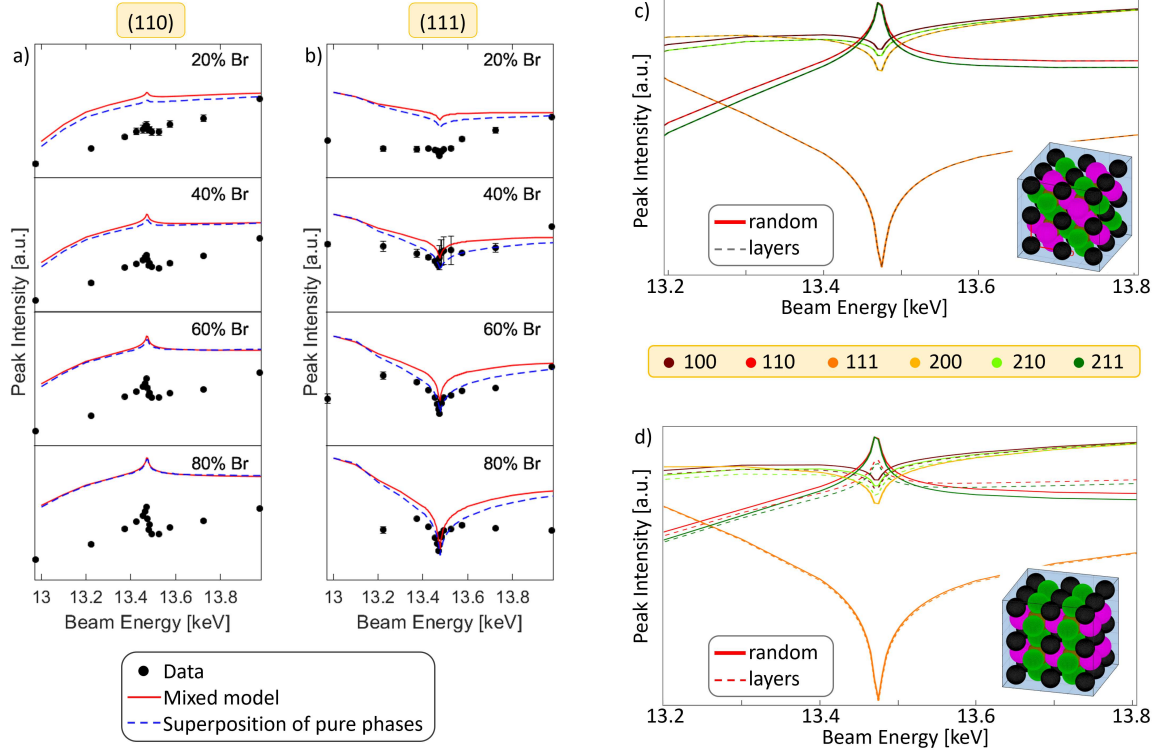
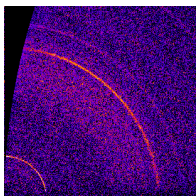


Figure 7.10: Normalized peak intensities of selected Bragg peaks as a function of beam energy around the bromine K-edge for MAPbBr_xI_{1-x} compositions. (a), (b) Displaying calculated data^{35,371-373} for a randomly mixed model and a superposition of mixed phases together with experimental data for compositions of $x = 0.2; 0.4; 0.6; 0.8$. (a) Intensity of the (110) diffraction peak (b) Intensity of the (111) diffraction peak. Calculated intensities for further diffraction peaks for the mixed model are shown in Figure D.5. (c), (d) Simulated intensities of various Bragg peaks comparing a randomly mixed model to layered arrangements of (c) diagonal layers, $x = 0.5$ and (d) vertical layers, $x = 0.33$. Insets in (c), (d) visualize the respective layered models. green spheres: iodide; pink spheres: bromide; black spheres: organic cation; brown spheres: lead. Numbers in the legend indicate Miller indices of the respective diffraction peaks.

Apart from mixing the metal cation, mixed halides are commonly applied for perovskite structures as introduced in Section 3.3 and detailed in Section 9.4. The mixing of halides in different ratios was investigated employing the bromide K-edge in MAPb(Br_xI_{1-x})₃ thin films, which is displayed in Figure 7.10. A distinct dependency of the magnitude



of the effect on the concentration of bromide is visible. The simulation in Figure 7.10 (a) and (b) assumes a random mixture of iodide and bromide throughout the material, both occupying the halide position within the perovskite structure in a randomly inter-mixed arrangement, comparing it to a model of two separate bromide and iodide-based phases. Since the expected differences are rather small, the experimental data does not allow an ultimate conclusion on the mixing behavior in this case. An ordering of the halide anions in different types of arrangements, as shown in Figure 7.10 (c) and (d), can be imagined as well. These ordered arrangements are expected to create distinct interference patterns between the ordered halides, modifying the intensity behavior of the anomalous effects. However, the calculations of the relative intensity variations for the different mixing models reveal that the expected effects do not alter the overall behavior of the peak intensities and only cause tiny deviations compared to the overall intensity trends. Since for all simulated models, the intensity trends for all signals are similar and the differences are minuscule, a distinction between the arrangements with a real-world experiment is challenging and cannot be achieved with the present data. An optimization of the experiment to such a high degree that these tiny variations can be distinguished is likely not feasible with the current setups due to possible systematic and statistical errors which are possibly much larger than the expected differences. These tiny variations between the anomalous diffraction effects for different mixing patterns, which are calculated theoretically, are considered to be caused by the fact that all potential positions for halides in a lead halide perovskite are equivalent and thus contribute each in a similar way and with the same scattering phase to the diffraction intensity. For materials containing non-equivalent positions within a unit cell, that can be occupied by two different kinds of ions, the differences for distinct mixing patterns are expected to be larger and measurable more reliably.

Besides the metal cation and the halide anion, the third component in hybrid halide perovskite structures is the central cation, which often is a molecular cation. However, since these are comprised solely of light elements such as carbon or nitrogen, anomalous diffraction around their absorption edges would have to be measured at very low X-ray energies, where absorption by all other components, including the surrounding air, would be high. Thus, generally, heavier elements are preferred for such experiments.

It has become common technique to replace or mix the organic cations with cesium or rubidium cations, as introduced in Section 3.2 and discussed in detail in Section 9.1. Due to their larger atomic mass, the absorption edges are expected at higher energies as listed in Table 7.1. For cesium, the L_I -edge at 5.71 keV is still relatively low, but nonetheless in the scope of many beamlines. Thus, mixed cation perovskite thin films employing the

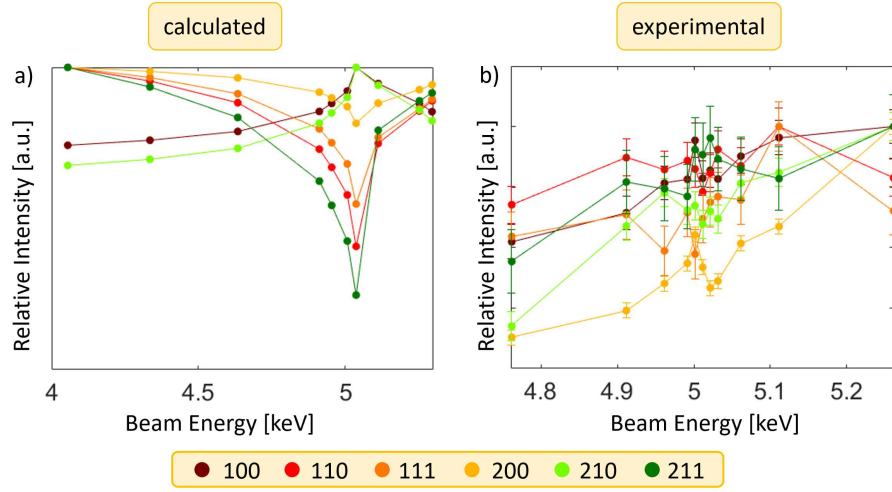
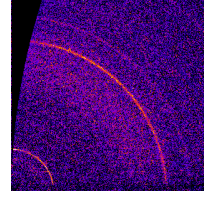


Figure 7.11: Normalized peak intensities of selected Bragg peaks as a function of beam energy around the cesium L_I -edge for $\text{Cs}_{0.2}\text{Rb}_{0.2}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.6}\text{PbI}_3$ thin films. (a) Simulated data,^{89,371} (b) experimental data. Numbers in the legend indicate Miller indices of the respective diffraction peaks. Raw data, i.e. reciprocal space maps and radial profiles of mixed cation samples are shown in Figure D.6 in the appendix.

widely applied mixture of $\text{MA}_{0.15}\text{FA}_{0.85}\text{PbI}_3$ with 20 % of cesium iodide inclusion were subjected to anomalous diffraction experiments around the cesium L_I -edge, which is displayed in Figure 7.11. As is visible there, no clear anomalous effect can be observed in the data. This is likely caused by different factors, including the possibility that cesium is not included into the perovskite structure in the desired crystallographic position, but it might likewise be possible that the included amount of 20 % is too low to be seen clearly. Additionally, the low X-ray energy leads to increased air absorption, generally lower transmitted beam intensity and reduced efficiency of the detector in this energy range, causing a considerable reduction of the detected intensity and thus lowering the signal-to noise ratio that might swallow the signal. Thus, experiments with improved parameters as well as higher amounts of cesium are required to possibly see the anomalous effect on cesium. This was however not the case of the presented experiment, where the objective was to determine whether cesium has been incorporated into the FA:MA composition in the given concentration. This can, however, not be answered with this kind of experiment.

For the slightly heavier rubidium cation, the energies of the absorption edges are much higher than for cesium, so it should be easier to measure and face less of the challenges due to low beam energy. However, as listed in Table 7.1, the rubidium K-edge, which would be in a convenient energy range for anomalous diffraction experiments practically

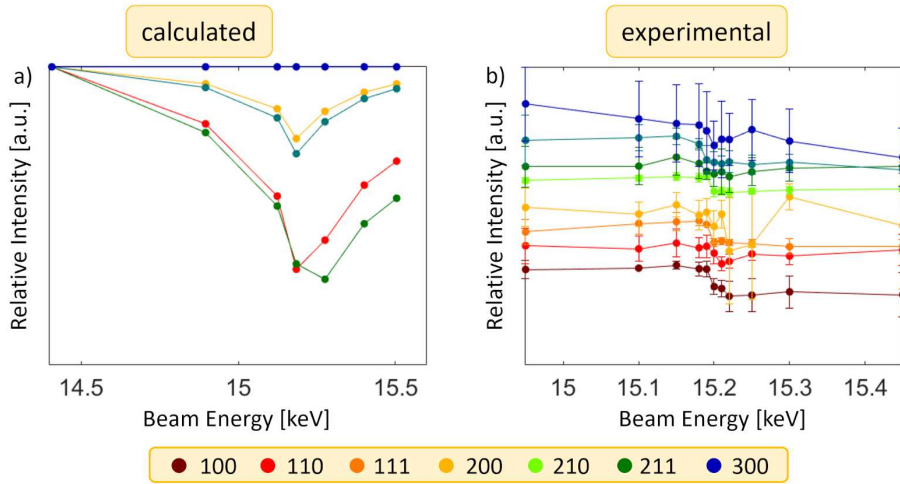
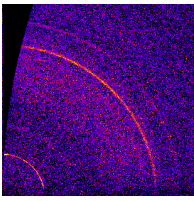
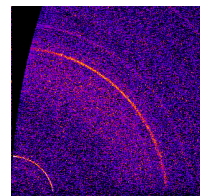


Figure 7.12: Normalized peak intensities of selected Bragg peaks as a function of beam energy around the rubidium K-edge for $\text{Cs}_{0.2}\text{Rb}_{0.2}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.6}\text{PbI}_3$ thin films. (a) Simulated data,^{89,371} (b) experimental data. Numbers in the legend indicate Miller indices of the respective diffraction peaks. Raw data, i.e. reciprocal space maps and radial profiles of mixed cation samples are shown in Figure D.6.

coincides with the lead L_{II} -edge. This lead edge is well-observed in anomalous diffraction experiments as presented above. In theory, a superposition between the effects of lead and rubidium on the intensity behavior should be observed. Thus, a possible route of resolving this issue could be the subtraction of the anomalous diffraction intensities of a reference $\text{MA}_{0.15}\text{FA}_{0.85}\text{PbI}_3$ sample without rubidium to eliminate the lead effect. This results in the data presented in Figure 7.12, which shows no detectable anomalous effect of the rubidium cation. That might relate to this method of simple superposition and subtraction not being applicable or, as for cesium, to the low amount of 20 % of rubidium that was applied in the current samples. Thus, these small amounts of alkali cations are likely not detectable by anomalous diffraction experiments. Lastly, as many reports state rubidium as immiscible into the FA:MA-based perovskite phase,^{145,176,177,180} it might simply not be present in the desired crystallographic position and thus not be detectable in the diffraction intensities of the perovskite phase at all. However, this conclusion cannot be drawn from the present data, since similarly to the cesium cation, the expected amounts of rubidium would be low and might not be detectable.

Thus, while in mixed compositions larger amounts of components ($\geq 20\%$ as shown for bromide above) in dedicated crystallographic positions can be successfully detected by anomalous diffraction experiments, this is likely the detection limit with the current setup.



CHAPTER 7. X-RAY TECHNIQUES

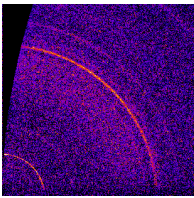
Conclusions Compared to standard ‘normal’ X-ray diffraction at X-ray energies distant from absorption edges, anomalous diffraction is a relatively infrequently used technique despite its potential to answer questions that cannot be resolved with standard diffraction. Thus, setups and measurements for anomalous diffraction are far from being optimized as much as other diffraction techniques and are possibly not meeting their theoretical potential. Since the power of anomalous diffraction has been demonstrated on other material types, more efforts are required to establish it as a technique to answer suitable questions on perovskite structures.

In this section it has been presented that it can be applied to detect certain elements in sufficient concentrations occupying distinct crystallographic positions. For small amounts, this is still challenging, but possible to overcome with optimization of measurement techniques. To elucidate mixing behaviors, the perovskite structure with its relatively high symmetry, in which all positions for a certain species (or mixture thereof) are equivalent, is possibly not well-suited. Instead, structures with reduced symmetry, such as layered structures, are expected to be more suitable.

Experimental Details Perovskite thin films for anomalous diffraction experiments were fabricated by the procedures detailed in Section C.2 (appendix) for the experiments on the tin and lead edges, in Section 9.4/publication [III] (lead acetate route) for the mixed halide thin films and in Section 9.1/publication [I] for the investigation of central cation mixing at the Cs/Rb edges. Anomalous diffraction experiments were conducted at beamline P23 of DESY (Hamburg, Germany), which provides an energy resolution of 1.3×10^{-4} and an accessible energy range of 5–35 keV. The samples were kept in a vacuum environment under a kapton dome during the experiment, while the beam path was in air. The detector distances were varied between 200–300 mm, while both a X-Spectrum Lambda 750K and a Dectris PILATUS3 X 1M detector were used to record two-dimensional diffraction pattern to include the diffraction intensities from differently oriented crystallites. Energy calibration was done using gold foil at the L_{II} and L_{III} edges (13.734 and 11.919 keV). Energy precision of the X-ray beam was 0.5 eV, the beam size was $300 \times 100 \mu\text{m}$.

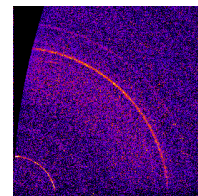
The lead L_{II} edge, tin K edge, bromine K edge, cesium L_I edge and rubidium K edge as listed in Table 7.1³⁷¹ were chosen for anomalous measurements. Measurements were performed at 15 energies around the chosen edge energy: ± 5 ; ± 10 ; ± 20 ; ± 50 ; ± 100 ; ± 250 ; ± 500 keV and the edge energy itself.

The data were then converted from angular space to q-space by self-written MATLAB scripts. Peak intensities were integrated by Gaussian fitting³⁷⁴ and tracked for different



Bragg peaks as a function of energy, while radial profiles (i.e. azimuthally integrated intensities) were used for randomly oriented samples to account for the intensity of the full diffraction ring, while for more spot-like peaks, separate integration wedges were applied. Data points were normalized to the monitor count. The increased background fluorescence above the absorption edge was employed as a baseline correction, while changing detector efficiency and X-ray absorption³⁵⁵ were accounted for by a linear model.

Energy-dependent diffraction patterns were simulated using the simulation mode of *Full-Prof.2k* in combination with MEADmaker³⁶⁶ based on crystal structures extracted from literature,^{35,89,156,372,373} while the energy dependent f' and f'' factors were interpolated from tabulated data.³⁷¹



Chapter 8

Perovskite Thin Film Fabrication

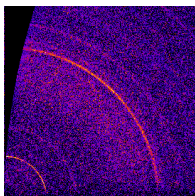
Samples in this thesis were produced by various methods, most frequently spin-coating, a solution based process, which is explained in the next section. Additional assistance for crystallization can be provided in the form of antisolvents or gas quenching to improve crystal quality and thin film morphology. Another approach is vapor deposition, where the precursors are directly evaporated and no solvents are involved. All of these techniques offer distinct benefits and challenges, which are explained in the following sections.

8.1 Spin-Coating

Spin-coating is an accessible and fast solution-based method to produce thin films. It allows to tune the deposition process by adjustable parameters such as spinning speed, acceleration and time. Furthermore, the surrounding atmosphere as well as the solution properties such as viscosity, solvent volatility and solute concentration affect the characteristics of the fabricated thin film. By careful adjustment of these parameters, the resulting films can be tailored in thickness and morphology, the latter of which can heavily depend on drying speed and the forces applied during spinning.

Briefly, the spin-coating process consists of four steps, as depicted in Figure 8.1: deposition of the solution, a first spinning step to flatten out the solution, a second spinning step, frequently applied at higher spinning speed, to form the thin film, and finally the evaporation of the solvent.³⁷⁵ A thorough description of the spin-coating process as well as the setup employed for the real-time experiments featured in this thesis can be found in the PhD thesis of Ekaterina Kneschaurek.³⁶³

To induce perovskite phase crystallization in as-deposited drying precursor thin films, a variety of quenching methods can be applied, such as antisolvent quenching or gas quench-



8.1. SPIN-COATING

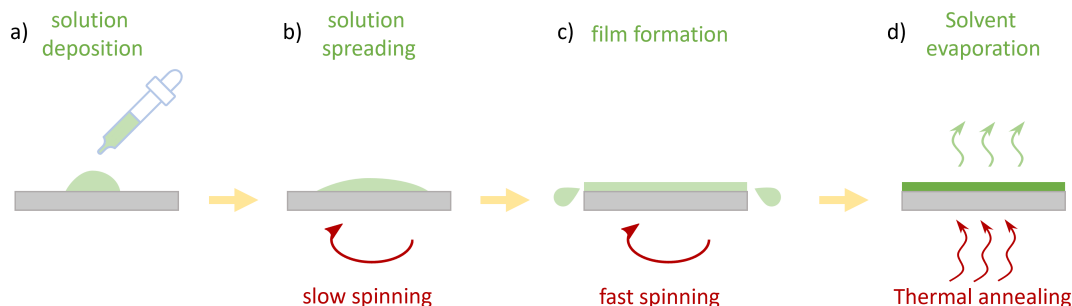
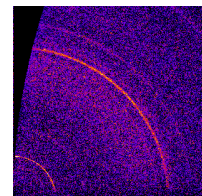


Figure 8.1: Schematic drawing of the spin-coating procedure consisting of several steps. (a) depositing the solution, (b) slow spinning to spread the solution, (c) fast spinning to form a thin film and to spin off superfluous solvent and (d) thermal annealing to evaporate the solvent and complete crystallization.

ing.^{280, 340, 376} These quenching techniques increase solvent drive-out speed as compared to simple drying of the deposited film, which generally results in improved film quality as described in the next sections.

Most perovskite compositions require additional thermal annealing after the spin-coating process to eliminate any solvent residues and crystallize the final material. For example, to create a cubic MAPbI₃ film, temperatures of 80 – 100 °C are required,^{34, 377–379} while FAPbI₃ requires even higher temperatures for the intermediary hexagonal phases to convert into a perovskite structure.^{380, 381} There are different approaches for annealing the thin film samples, the most widespread of which are hotplate heating and radiative thermal annealing.



8.2 Solvent Engineering — Antisolvent Quenching

Additional to thermal annealing, high efficiency perovskite materials have been produced by employing the so-called antisolvent technique - a solvent exchange-based approach to facilitate crystallization of the perovskite material.^{376,382} Usually, the antisolvent is applied during the spin-coating, which is schematically depicted in Figure 8.2. An antisolvent with orthogonal solubility properties to the precursor solvent is added to the wet film, inducing a rapid supersaturation and precipitation of crystalline perovskite material. Thin films fabricated using antisolvents have been found to possess differing morphologies than those purely produced by thermal annealing^{278,336,376,381} as well as generally higher device efficiencies.^{336,376} Importantly, antisolvent methods are not limited to spin-coating, but can be applied together with further solution-based deposition methods as well. It has been shown, however, that parameters, such as antisolvent deposition time and speed as well as the type of antisolvent can play a crucial role in final film morphology and device performance.^{382,383} A narrow time window limits the flexibility of the process: the antisolvent has to be added before any crystalline intermediate forms. Once crystalline solvent complexes are formed, antisolvent cannot remove the solvent molecules from the structure, but conversion into perovskite can only happen thermally. On the contrary, if the antisolvent is added too early, it is not able to induce sufficient supersaturation.^{295,337} Therefore, antisolvent addition requires accurate timing in order to induce supersaturation and homogeneous nucleation. Finally, the antisolvent deposition method can influence the final film properties as well, as illustrated in Section 12.1.

Although the antisolvent method is the most widespread quenching technique for fabricating perovskite thin films, there are certain drawbacks, including the already mentioned narrow application time window and concomitant impediments for reproducibility as well

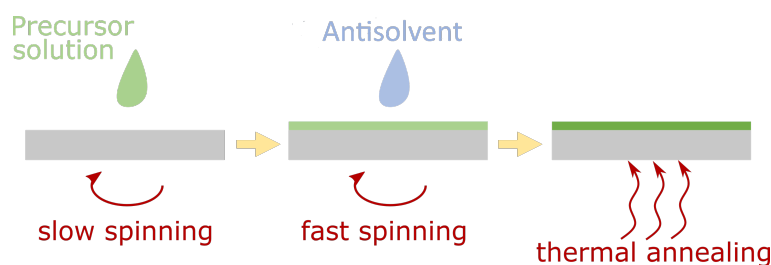
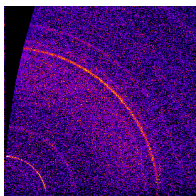
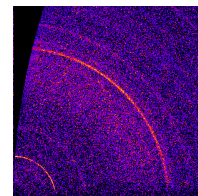


Figure 8.2: Schematic depiction of the antisolvent-assisted deposition procedure. After an initial slower spinning step, antisolvent is dropped onto the fast spinning sample to induce crystallization.



8.2. ANTISOLVENT

as usage of often highly toxic antisolvents, such as the most widely used antisolvent chlorobenzene, and a large amount of waste. To combat these, alternatives such as gas quenching are employed, which is described in the next section.



8.3 Gas Quenching

An alternative to applying an orthogonal solvent during the spin-coating of perovskite thin films is directing an inert gas flow onto the spinning substrate,^{105,145,280,340,384} as schematically depicted in Figure 8.3. Although in principle any inert gas could be applied, usually nitrogen is chosen.

In general, gas quenching serves a similar overall purpose as applying an antisolvent, to remove the original solvent from the thin film during deposition to induce supersaturation and crystallization. In this case, the strong gas-flow leads to increased evaporation of the parent solvent. The gas quenching technique has shown to be more robust than the antisolvent technique towards variations in processing parameters such as deposition times.²⁸⁰ This increases reproducibility and adaptability for different deposition setups and methods, as well as creating less environmental hazard by replacing toxic antisolvents with nitrogen.

Despite the clear advantages of gas quenching, it is not nearly as popular as the antisolvent technique, but holds a huge potential for more sustainable and environment-friendly deposition routes.

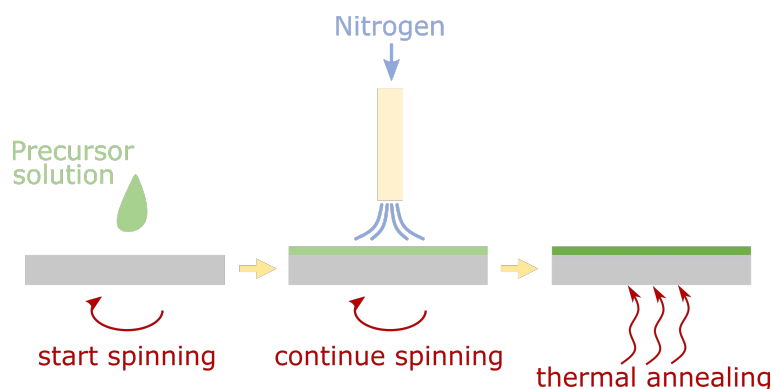
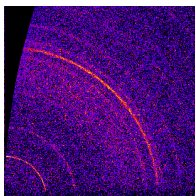


Figure 8.3: Schematic depiction of the nitrogen gas quenching-assisted deposition procedure. A nitrogen flow is directed onto the spinning sample to induce crystallization.



8.4 Vapor Deposition

Eliminating solvents completely can be achieved by applying vapor-based processes. Those generally enable a high level of control and material purity, but require complex set-ups, long reaction times and energy-intensive evaporation processes.^{278,385} Despite these processes offering distinct advantages, including compatibility with different types of substrates, transport layers and stacked architectures due to eliminating the danger of solvent damage,³⁸⁶ the required complex infrastructures and high energy processes seriously hamper the potential for industrial utilization.

In research laboratories, vapor-based techniques are widely applied, often in the form of multi-source co-deposition, where rate control allows facile compositional tuning.^{231,386} Single-source evaporation of pre-formed compounds or chemical vapor deposition employing auxiliary inert gases are alternative vapor-based techniques.³⁸⁷

In this thesis, vapor-based deposition methods for perovskite thin films play a minor role, and vapor-deposited structures are featured in Section 12.2. The thin films therein are fabricated by multi-source co-evaporation, which enables formation of delicate multi-layered thin films as well. A schematic depiction of a setup for dual-source co-deposition of a perovskite thin film is found in Figure 8.4.

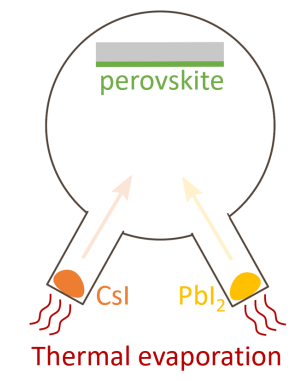
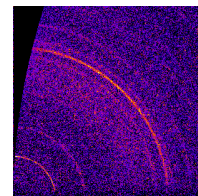


Figure 8.4: Schematic depiction of CsPbI_3 perovskite thin film deposition by dual-source co-evaporation.

III RESULTS AND DISCUSSION

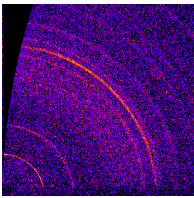


Chapter 9

Effects of Component Mixing on the Structure, Properties and Growth of Perovskite Thin Films

This chapter presents the results of structural investigations on perovskite thin film materials with varying composition. Herein, as well as in the following chapter, materials exhibiting the classical perovskite structure featuring a three-dimensional network of lead halide octahedra are discussed, while layered structures are discussed in Chapter 11. The present chapter focuses on the structural and material properties as a function of material composition. In Section 9.1, the effect of mixing smaller cations such as alkali cations into formamidinium-based perovskite thin films is elucidated. An alternative approach of incorporating these smaller cations only partially on the surface of thin films to create gradient structures is discussed in Section 9.2. Furthermore, Section 9.3 discusses the effects of incorporating a larger cation on the example of imidazolium.

Since not only for the central cation mixed compositions can be applied, the final section of this chapter, Section 9.4, discusses mixed halide perovskite thin films.



9.1 Quantifying Stabilized Phase Purity in Formamidinium-Based Multiple-Cation Hybrid Perovskites

This section is based on publication [I]. Therein, the effect of mixing cations on the phase purity of perovskite materials is investigated in a quantitative approach. The study focuses on investigating and quantifying the effects of cation mixing on the crystal structure of perovskite thin films. A simple and non-destructive method for quantifying the phase composition by GIWAXS analysis is introduced. It can and has in the meantime been employed for investigating thin films in-situ as well, i.e. during film fabrication.^{23,24,357,388} This section serves as an overview on the power of the GIWAXS analysis and the ample amount of information it can provide. Finally, the structural findings are connected to the device performance of the respective thin films, to underline the relevance for photovoltaics research.

As the base material, formamidinium lead iodide (FAPbI₃) is chosen, which is widely investigated as an alternative absorber material to methylammonium lead iodide (MAPbI₃), due to the potentially higher thermal³⁷ and environmental^{138,159,161} stability of the formamidinium ion as compared to methylammonium. Additionally, a narrower band gap of the FAPbI₃ perovskite could enable a larger fraction of solar energy harvesting.^{37,87} However, at room temperature the stable phase of FAPbI₃ adopts a hexagonal non-perovskite structure, which is not suitable for solar cell devices, since it is photoinactive.^{35,87} Thus, stabilizing the photoactive perovskite phase of FAPbI₃ at room or working temperature has been a challenge that received a lot of attention by the perovskite photovoltaics research community.^{94,243}

A common technique is tolerance factor tuning by mixing formamidinium with smaller cations such as cesium or rubidium as introduced in Section 3.2. For this study, four sample compositions are chosen: the parent compound, containing a mixture of 83 % FAPbI₃ and 17 % MAPbBr₃, called **FA:MA** in the following; a similar composition with the addition of 10 % of excess PbI₂, referred to as **excess PbI₂**; a triple mixture of FA⁺, MA⁺ and Cs⁺ cations, where 5 % of CsI is added to the FA:MA precursor solution, called **FA:MA:Cs**; and the quadruple composition of FA⁺, MA⁺, Cs⁺ and Rb⁺, where an additional 5 % of RbI is added to the precursor solution, called **FA:MA:Cs:Rb** in the following. The triple and quadruple cation compositions feature a 10 % excess of PbI₂ as well.

The thin films were prepared prior to the experiment by spin-coating from solutions in

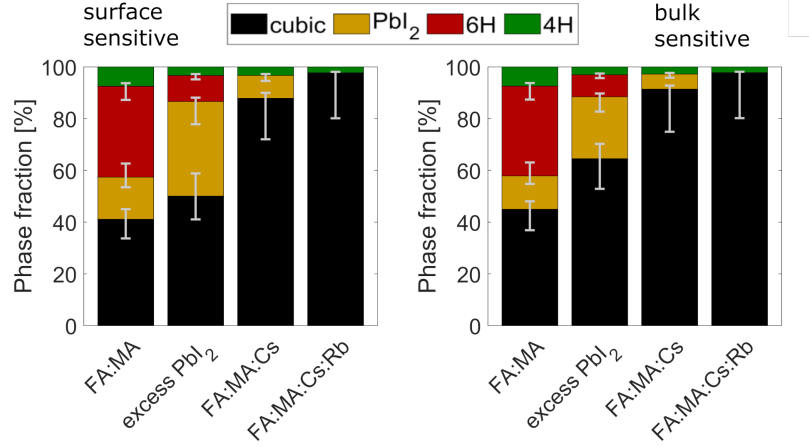
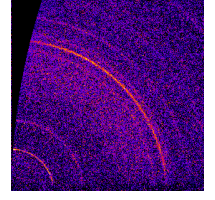


Figure 9.1: Molar phase fractions of cubic perovskite, hexagonal δ -FAPbI₃, and PbI₂ phases depending on the film composition, as determined from peak integration of radial intensity profiles extracted from reciprocal space maps at incidence angles of 0.1° (left, surface-sensitive) and 0.2° (right, bulk-sensitive). Error bars were estimated due to compositional uncertainties and experimental statistics. Image taken from publication [I].

anhydrous DMF:DMSO 4:1 (v/v). Details on thin film and device fabrication can be found in publication [I].

Phase Composition of Mixed Cation Perovskite Films It can be observed that the presence of impurity phases is largely determined by the cation composition, as summarized in Figure 9.1. The FA:MA composition features the hexagonal polytypes 4H and 6H^{89,90} next to the perovskite phase and a PbI₂ phase. Adding an excess of PbI₂ significantly reduces the amount of both hexagonal polytypes, increasing the perovskite fraction, but expectedly increases the amount of PbI₂ phase. Adding cesium cations into the composition eliminates the 6H polymorph, only leaving a small amount of 4H phase and PbI₂ next to the perovskite phase. Further improvement of phase purity can be reached when adding rubidium cations to create a quadruple cation composition, eliminating the excess PbI₂ phase as well, and further reducing the presence of 4H phase to create a thin film consisting almost exclusively (98 %) of perovskite phase. This is considered to be due to the joint effects of the cesium and rubidium cations, such that the presence of cesium suppresses the hexagonal phase during the crystallization^{183,292,293} and rubidium reduces the PbI₂ impurities.^{389,390}

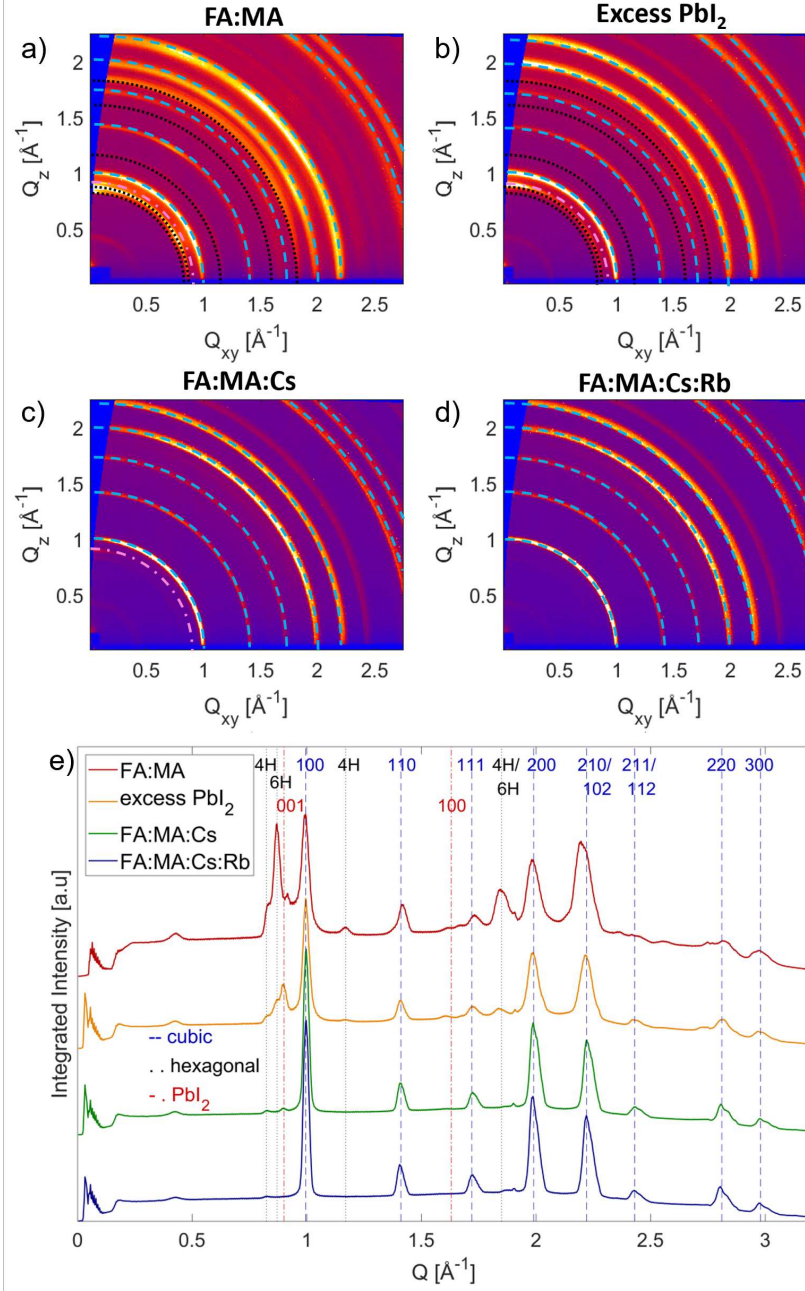
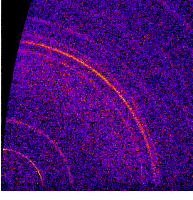


Figure 9.2: (a) – (d) GIWAXS reciprocal space maps of perovskite thin films with different compositions. Ring-shaped diffraction features indicate a random orientation of perovskite crystallites. Blue-dashed lines mark perovskite signals, hexagonal phases are labeled in black, and PbI_2 is denoted by pink lines. The incidence angle is 0.14° for acquisition of all reciprocal space maps. (e) Radial intensity distribution extracted from reciprocal space maps. Peaks are indexed according to literature,⁸⁹ displaying a cubic perovskite crystal structure. Additional hexagonal⁸⁹ and PbI_2 phases³⁹¹ can be found for certain samples, as detailed in the text. Image taken from publication [I].

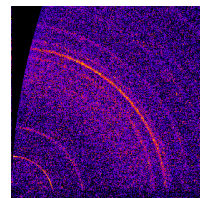


Figure 9.2 shows GIWAXS reciprocal space maps for all samples, together with radial profiles in Figure 9.2 (e), where the intensity variations and disappearances of diffraction signals belonging to the respective phases can be seen when altering the material composition. Quantification of the phase composition was done by peak integration (for overlapping peaks, multi-peak fitting was performed) and scaling by structure factors. Lorentz and polarization correction factors were considered in the calculations, as well as the multiplicity and unit cell volumes to calculate molar phase fractions of the different structures, the values of which are represented in Figure 9.1. For the structure factor calculation, tabulated atomic form factors were used³⁵¹ and the positions of atoms/ions within the unit cell were obtained from literature.^{89,391} Orientational differences for the different phases were accounted for by geometric correction factors. Especially PbI_2 exhibited a more strongly pronounced orientational order compared to the perovskite phase, indicated by a localized signal close to the z -axis in the reciprocal space map (e.g. as marked by a red dot-dashed line in Figure 9.2). The perovskite signals exhibit a ring shape in all reciprocal space maps in Figure 9.2, marked by light blue dashed lines, which is indicative of randomly oriented crystallites. Recording a two-dimensional GIWAXS reciprocal space map instead of performing standard X-ray diffraction in reflection geometry enables detection of both the vertically oriented and non-oriented phases and components of the sample simultaneously and determine their degree of orientational order as well.

Structural Properties and Phase Distribution Azimuthal profiles of the perovskite (110) signal are shown in Figure 9.3 as a representation of the orientational order within the perovskite phase. A completely randomly oriented material would exhibit uniform intensity along the whole diffraction ring, resulting in a flat line for the azimuthal profile. Distinct maxima, as can be most clearly seen for the (110) signal of the FA:MA sample, indicate a notable degree of oriented crystalline domains. The preferred orientation of the (110) diffraction plane along 60° relative to the surface is consistent with the previously reported preferred alignment of the (202) plane parallel to the substrate.²⁰ Adding excess PbI_2 , as well as CsI and RbI, reduces the amount of preferred orientation as can be seen from the distinctly reduced maximum in the azimuthal intensity curves of the respective samples.

Another major advantage of GIWAXS is the possibility to tune the probing depth by adjusting the grazing incidence angle. This leads to a variability of surface sensitivity to probe exclusively the film surface or include the bulk material as desired. This provides the possibility to compare surface and bulk properties. Figure 9.1 represents the phase compositions on the sample surface and in the bulk, respectively. For surface sensitive

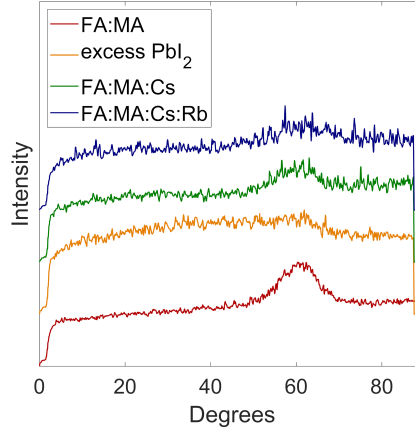
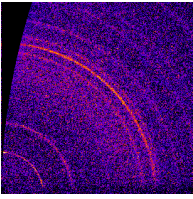


Figure 9.3: *Intensity of the (110) diffraction signal as a function of azimuthal angle. Only for this crystallographic plane a clearly preferred orientation can be found, which is most pronounced for the FA:MA sample. Incidence angle is 0.14° . Image taken from publication [I].*

analysis, an incidence angle of 0.1° was applied, which is close to the critical angle of the sample material, while for bulk analysis an incidence angle of 0.2° was employed. The trends in phase fractions for different cation compositions as described above are consistent for the film surface and the bulk. However, especially for the PbI_2 phase, a higher fraction can be observed close to the surface than in the bulk. This is consistent for all samples containing a PbI_2 phase, which implies that this PbI_2 phase is located preferably on the surface of the film. The greater prevalence of PbI_2 on the surface as compared to the bulk of the film is likely a result of a greater vulnerability of the surface towards material degradation since PbI_2 is a common degradation product of lead halide perovskite materials.^{158, 159, 346, 392} Consequently, the fraction of perovskite phase is higher in the bulk of the material as compared to the surface due to the reduced prevalence of PbI_2 there. Hexagonal polytypes, on the other hand, are almost uniformly distributed throughout the depth of the film, as indicated by very similar phase fractions on the surface and in the bulk.

Improved purity of the perovskite phase upon cation mixing is suggested by the disappearance of the signals that were ascribed to impurity phases, i.e., PbI_2 and hexagonal polymorphs. Furthermore, a general peak sharpening can be observed, indicative of an improvement in crystal structure by enhanced size of the coherently scattering domains. Figure 9.4 (a) shows the domain size as a function of composition as determined from the peak width (FWHM) of X-ray reflectometry (XRR) data (Figure D.7, appendix), which is consistent with an observed peak sharpening in the reciprocal space maps in Figure

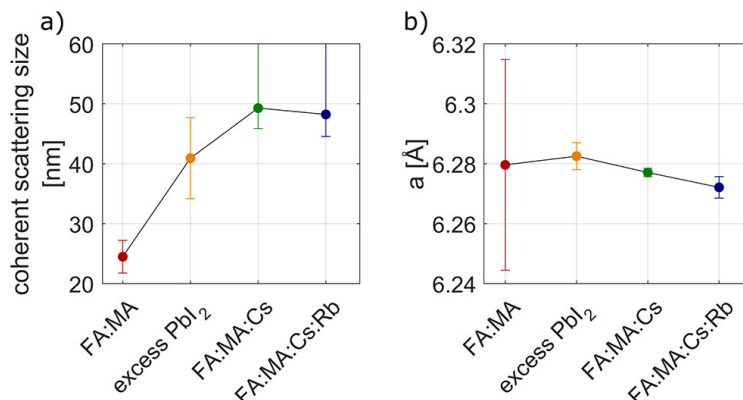
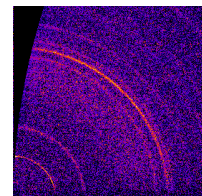
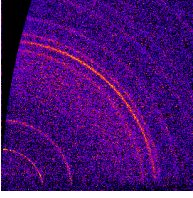


Figure 9.4: (a) Minimum coherently scattering island size as a function of composition, determined from Gaussian fits of peak widths (FWHM) of X-ray reflectometry data (Figure D.7, appendix). Averaging was performed over different crystallographic directions, as similar trends could be observed for all of them. (b) (Pseudo-)cubic unit cell parameter a as a function of composition, determined from Gaussian fits of peak positions observed in the X-ray reflectometry data. Image taken from publication [1].

9.2. It can be seen that adding excess Pbl₂ already increases the domain size, while the presence of cesium and rubidium increases the coherently scattering domains, and along with that suggests larger crystallites, by a factor of two or more. A significant difference between the domain sizes of triple and quadruple cation materials can not be observed, which is, however, ascribed to the limited resolution of the setup.

Inorganic Cation Incorporation A question still under debate is, whether the rubidium cation can actually be incorporated into a lead halide perovskite composition based on MA⁺ and FA⁺,^{145, 172, 176, 177, 180, 393–396} while on the incorporation of cesium cations a broad consensus has been achieved.^{170, 176, 177, 180, 397} To address the question of cation incorporation, lattice parameters of the perovskite structure, assuming a cubic symmetry, were determined for the different compositions. Figure 9.4 (b) depicts the cubic unit cell parameter a as a function of composition. Data from XRR (Figure D.7, appendix) was used to calculate the unit cell size from the positions of the diffraction signals. From the calculated lattice parameters, it can be observed that excess Pbl₂ leads to a small increase in the unit cell size compared to the MA:FA mixture, which can be considered to be caused by partial substitution of bromide ions in the mixed composition with the larger iodide ions. Addition of cesium cations slightly shrinks the lattice, suggesting incorporation of the smaller inorganic cation in the hybrid perovskite, partially substituting for the larger organic cations FA⁺ and MA⁺ and thus decreasing the effective average cation radius.



9.1. MULTIPLE CATIONS

Upon introduction of rubidium cations into the material, a still smaller unit cell size is observed. Besides possible incorporation of the smaller rubidium cation into the perovskite lattice, there may be several possible reasons for that. The rubidium cation has been found to interact strongly with iodide, leading to the formation of rubidium and iodide-rich side phases^{176, 181} and increasing the bromide ratio in the perovskite phase, which is expected to cause a smaller lattice constant as well. Furthermore, since the presence of cesium cations has been observed to influence the distribution of rubidium cations in the film,¹⁷² the presence of rubidium cations might reversely alter the distribution of the cesium cations in the material as well. The apparent lattice contraction upon RbI incorporation potentially can be ascribed to those side effects and does neither provide sufficient proof for an incorporation into the perovskite structure, nor for the opposite.

Photovoltaic Properties The effect of compositional engineering and the resulting structural variations on the photovoltaic properties of the respective materials was investigated under standard illumination conditions. Details on device fabrication and analysis can be found in the experimental section of publication [I]. The summarized current-voltage characteristics in Figure 9.5 (a) and Table 9.1 show that the power conversion efficiency (PCE) of the material increases when adding excess PbI_2 , which is a result of an increase in all measured photovoltaic parameters, including open circuit voltage (V_{OC}), short circuit current (J_{SC}) and fill factor (FF). Their increase is most likely due to an increased amount of photoactive perovskite phase as compared to the reduced amount of photoinactive hexagonal polymorphs. Incorporation of cesium cations further enhances all photovoltaic parameters, as summarized in Table 9.1, which again correlates with an increased fraction of photoactive phase in the material. In contrast, rubidium cation addition mainly increases the V_{OC} , but not the J_{SC} .

Table 9.1: Summarized photovoltaic parameters, including open circuit voltage (V_{OC}), short circuit current (I_{SC}), fill factor (FF) and power conversion efficiency (PCE) for perovskite thin films with different compositions.

	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
FA:MA	1.042	16.3	67.7	11.74
Excess PbI_2	1.104	21.22	75.3	18.0
FA:MA:Cs	1.134	22.72	76.0	20.1
FA:MA:Cs:Rb	1.161	22.28	76.8	20.24

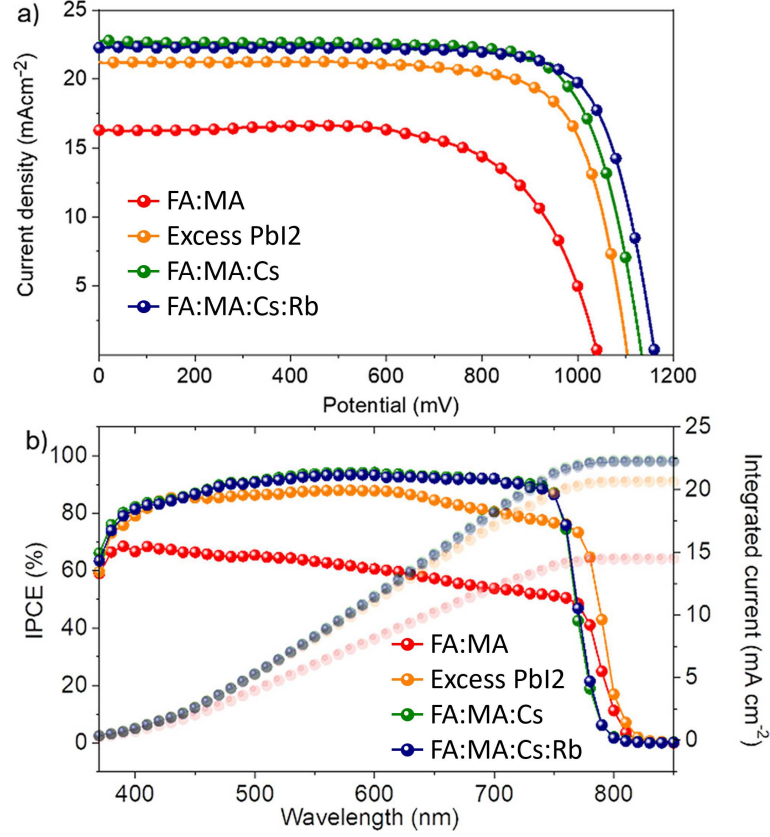
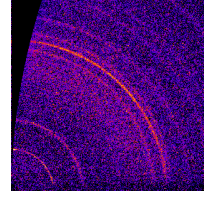
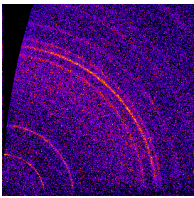


Figure 9.5: (a) Current density-voltage (J - V) characteristics measured under standard simulated AM1.5 illumination at a scan rate of 100 mV/s (reverse scan, with an illumination area of 0.16 cm²) corresponding to devices based on the following architecture: FTO/c-TiO₂/m-TiO₂/Perovskite/spiro-OMeTAD/Au. (b) Incident photon-to-current conversion efficiency (IPCE) as a function of the monochromatic wavelength recorded for devices with different compositions and the integrated current density obtained from the respective IPCE spectrum. Image modified from publication [I].

These results are further corroborated by the incident photon-to-current conversion efficiency (IPCE) spectra presented in Figure 9.5 (b), where the IPCE is shown as a function of illumination wavelength. The absorption (and therefore photocurrent) onset at high wavelengths which corresponds to the band gap of the material occurs at a slightly smaller wavelength when incorporating cesium, indicating an increase in the band gap with respect to the double cation composition, as would be expected upon incorporation of the smaller cesium cation. Addition of rubidium into the material, however, does not alter the IPCE onset, and therefore band gap, further, which indicates that it is indeed not incorporated into the main photoactive perovskite material but rather plays a role in reducing impurity phases in between perovskite grains. Comparing the material with excess PbI₂



9.1. MULTIPLE CATIONS

to the stoichiometric FA:MA mixture, no shift in the band gap value is observed, which matches expectations, since the composition of the main photoactive material should not be greatly altered, solely its ratio in the final film.

Band gap trends were confirmed by steady state photoluminescence (PL) spectroscopy (Figure 9.6 (a)), which shows that FA:MA and excess PbI_2 thin films present the same emission energy. Adding cesium cations shifts the PL maximum to higher energies, consistent with an increased band gap, while additional admixture of rubidium cations does not exert a significant effect on the steady state PL.

Time-resolved PL analysis (Figure 9.6 (b)) was performed to investigate charge carrier lifetimes, which can be extracted from the decay time of the PL intensity as τ_{10} , the time when the PL intensity drops by an order of magnitude. It can be seen that upon excess

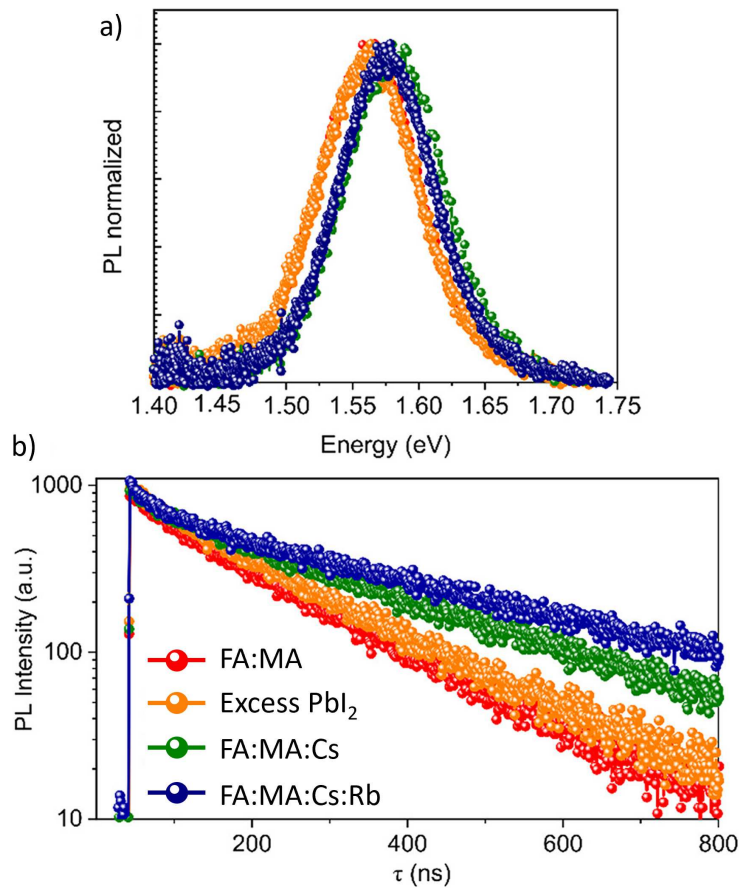
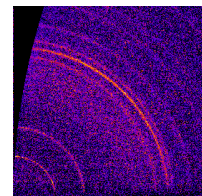


Figure 9.6: (a) Steady-state photoluminescence (PL) spectra showing widening of the band gap with the introduction of cesium cations and (b) time-resolved PL studies performed on samples with different compositions. The charge carrier lifetime increases in triple and quadruple-cation-based perovskite samples. Image taken from publication [1].

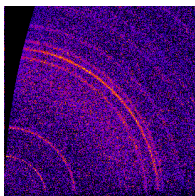


CHAPTER 9. COMPONENT MIXING

PbI_2 addition, the decay speed only slightly reduces, implying a slight reduction in charge carrier recombination. Upon cesium and rubidium cation addition, τ_{10} increased from 430 ns to 600 ns and 770 ns, respectively, indicating longer lived carriers. Their presence infers the reduction in non-radiative recombination, which is considered to be due to the increased phase purity in the perovskite thin film and the increased crystallite size.

Conclusions In summary, a detailed investigation and quantification of the effects of mixing multiple cations in a hybrid lead halide perovskite including excess lead iodide conditions were conducted. The distinct effects of mixing the organic cations formamidinium and methylammonium as well as the inorganic cations cesium and rubidium were displayed. The specific effects on the structural properties of the materials, such as phase composition, orientational order, domain size and crystal structure could all be revealed by non-destructive X-ray diffraction methods including GIWAXS and XRR. These structural properties were then related to the photovoltaic parameters of devices built from the respective materials. Thus, by structural investigations, already many of the variations in photovoltaic performance can be explained and predicted.

This study can therefore serve as an example how X-ray diffraction, as an accessible and non-destructive method to quantify the phase composition and here first of all GIWAXS due to its fast acquisition of large q-space ranges, can be employed in perovskite and photovoltaics research, even offering the possibility to monitor processes in real time to adjust the processing conditions for optimization of the structural thin film properties, which greatly influence the photovoltaic performance.



9.2 Host-Guest Complexation of Cesium Cations for Fabrication of Gradient Structures

In the previous section, cation mixing is presented as a strategy to tune and stabilize perovskite materials, especially formamidinium lead iodide (FAPbI₃), where alkali cation admixture has shown to stabilize the photoactive perovskite phase. However, bulk cation mixing implicates potentially undesired side effects, such as a band gap increase.^{170,393,396} Additionally, further drawbacks such as defects and impurities that facilitate non-radiative recombination of charge carriers are not addressed and are possibly even increased by bulk cation mixing.³⁹⁶

Thus, this section focuses on the approach of gradient doping on the thin film surface by delivering cesium cations via a host-guest complexation strategy. The section is based on publication [II].

Herein, the multimodal host-guest complexation strategy is developed by employing a crown ether, dibenzo-21-crown-7, which acts as a transporting agent for delivering cesium cations to the surface of a FAPbI₃ thin film to establish a gradient doping profile by infusion of the base material with cesium cations. The key of applying a complexation strategy for post-depositional treatment of perovskite thin films is that instead of polar solvents, which are usually used to dissolve alkali salts, but readily dissolve perovskite thin films as well, an orthogonal non-polar solvent can be applied with a crown ether. Macrocyclic crown ether molecules are highly soluble in such non-polar solvents and are able to transfer specific metallic ions into this solution by formation of host-guest complexes via ion-dipole interactions between the oxygen atoms of the macrocycle and the metal

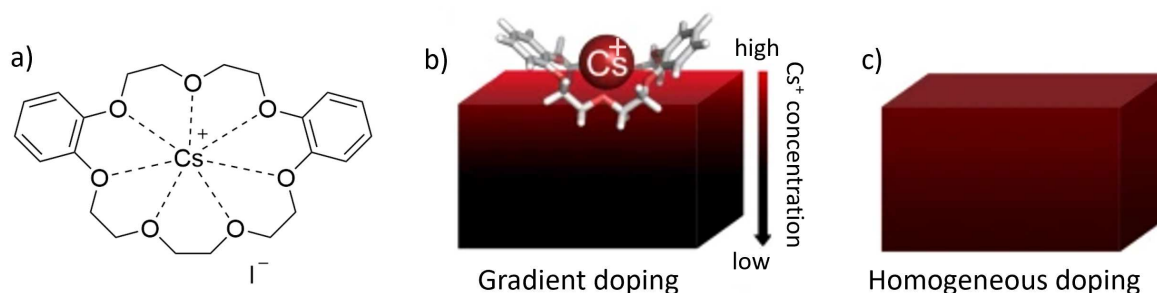
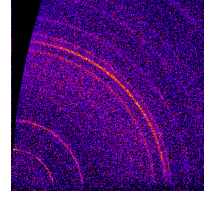


Figure 9.7: (a) Molecular structure of the CsI-dibenzo-21-crown-7 complex. (b) and (c) Schematic representation of the (b) gradient and (c) homogeneous cesium doping of perovskite films. Image modified from publication [II].



cations.^{398,399} The applied dibenzo-21-crown-7 (shown in Figure 9.7 (a)) forms specific complexes with the cesium cation due to their complementary size. This way, it can be applied to deliver and infuse cesium cations into the surface of a perovskite thin film. With this strategy, not only a gradient doping profile is created, which is expected to assist in photoinduced charge carrier separation, but the number of surface and bulk defects is reduced as well, and the thin film morphology is improved. The vacated crown ether even provides the potential to assist in binding lead ions and reducing their environmental hazard.

Surface Modification of Perovskite Thin Films Perovskite thin films based on FAPbI_3 and $(\text{FAPbI}_3)_{0.97}(\text{MAPbBr}_3)_{0.03}$ were deposited by an antisolvent method as described in the experimental section of publication [II]. The crown ether complex was synthesized from dibenzo-21-crown-7 and a CsX salt with $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ as detailed in the experimental section of publication [II]. The as-deposited perovskite thin films were then treated with the solution of the crown ether complex by covering them with the solution for 2 s, followed by spin-coating and subsequent annealing to promote infusion

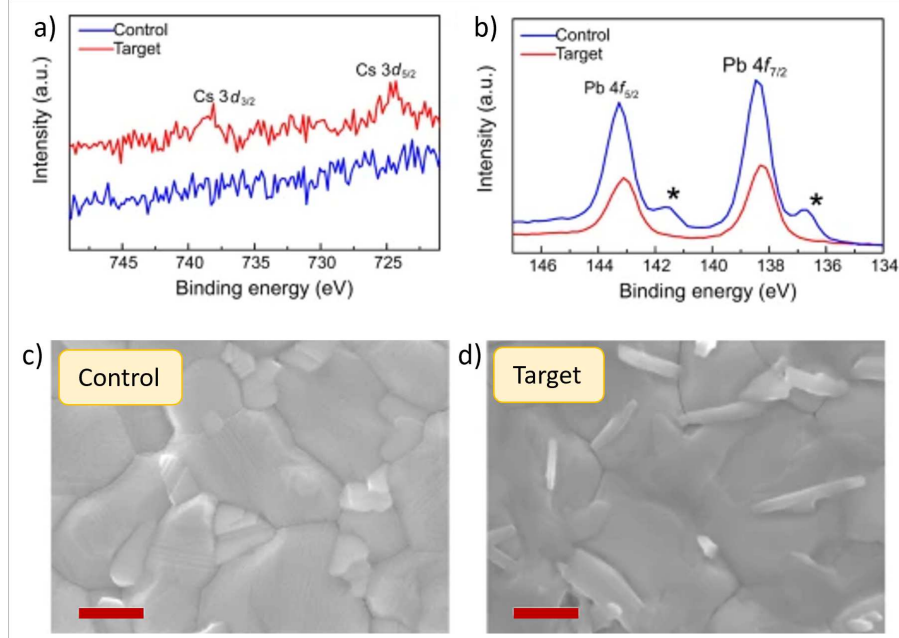
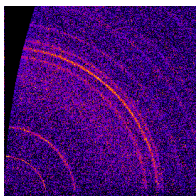


Figure 9.8: Core-level X-ray photoelectron spectra for (a) $\text{Cs } 3d$ and (b) $\text{Pb } 4f$ orbitals. The asterisks indicate metallic Pb species. Top-view scanning electron microscopy images of (c) control and (d) target perovskite films revealing surface nanostructures upon treatment of the surface with the solution of the crown ether complex. The scale bar represents 500 nm. Image modified from publication [II].



of the Cs^+ ions into the perovskite material to create a graded composition as shown schematically in Figure 9.7 (b).

The presence of cesium on the film surface after treatment with the solution of the crown ether complex was verified by X-ray photoelectron spectroscopy (Figure 9.8 (a), for details, see publication [II]), which is absent in untreated samples. Instead, signals associated with metallic lead species are found, which are not visible in the spectrum of the surface modified perovskite film (Figure 9.8 (b)). This indicates a reduction of metallic lead species, likely by the crown ether binding to the undercoordinated Pb^{2+} , which is assumed to be responsible for the formation of metallic lead. Since metallic lead has shown to hamper the photovoltaic performance and stability of perovskite thin films,⁴⁰⁰ this reduction likely benefits the operational parameters.

Analysis by scanning electron microscopy (SEM, Figure 9.8 (c) and (d)) of the surface of crown ether complex treated and untreated perovskite films reveals the presence of needle-like structures only on the treated films, which are tentatively ascribed to a surface species containing the crown ethers. Additionally, the apparent number of grain boundaries is observed to be greatly reduced after surface treatment along with an increased grain size. A clear modification of the electronic structure on the surface of perovskite thin films treated with the crown ether complex can be observed as well, see publication [II] for details.

Structural Properties of Surface Modified Thin Films To elucidate on the structural properties and their modification upon surface treatment by the crown ether complex, GIWAXS analysis was performed (Figure 9.9). Comparing the reciprocal space maps of the surface of cesium-infused (Figure 9.9 (c)) and untreated (Figure 9.9 (a)) thin films, it is apparent that the untreated film features significantly more impurity phases such as PbI_2 , as marked in the image, and in some cases even hexagonal polymorphs of FAPbI_3 (see appendix, Figure D.8 (a)). In the treated films, those cannot be detected, indicating on the one hand a stabilization of the perovskite α -phase of FAPbI_3 against the hexagonal polymorphs and on the other hand a possible protective effect against material degradation as well, a result of which is often PbI_2 .^{158, 346}

New signals appear for the sample treated with the crown ether complex in the q -region below $0.5 \text{ \AA}^{-1}$, which are marked in Figure 9.9 (c) with a green circle. These signals were ascribed to a surface species containing the crown ether complex. A powder of the crown ether complex has been crystallized, which showed a broad signal in its powder diffraction pattern (Figure D.9 (a), appendix) that correlates to the signals observed in the GIWAXS data. Density functional theory (DFT, see Figure D.9, appendix) optimization of a gen-

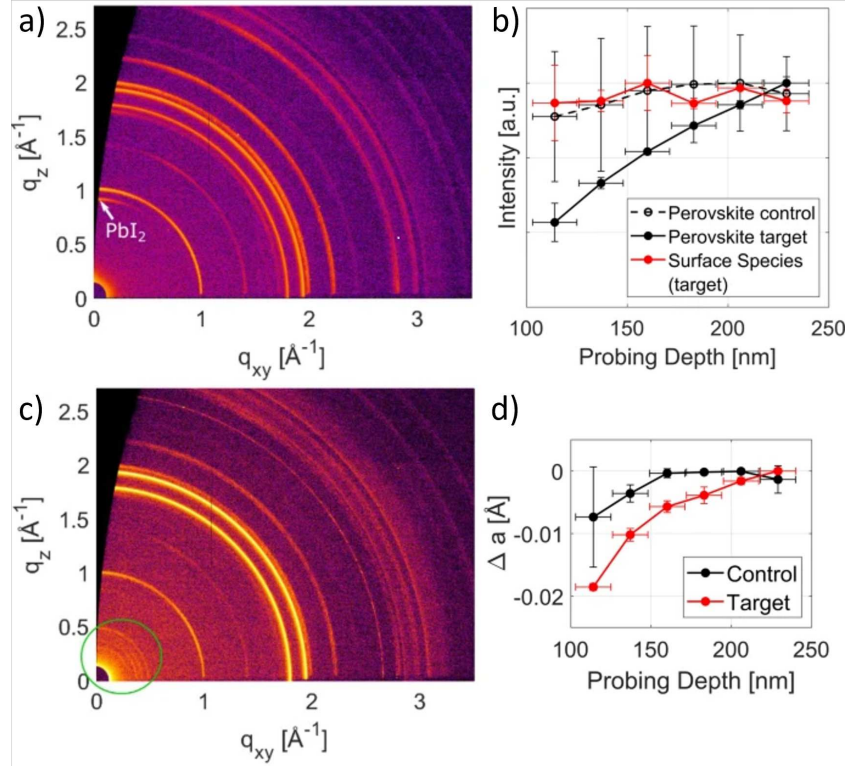
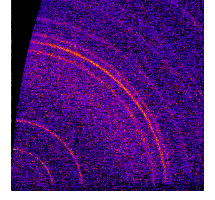
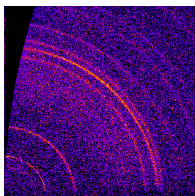


Figure 9.9: Structural characterization of perovskite thin films. GIWAXS reciprocal space maps of (a) control sample, (c) sample treated with crown-ether complex (target sample) at an incidence angle of 0.12° , probing the surface of the material. Low q signals of the surface species are marked with a green circle. (b) Peak intensities of different crystal phases as a function of the estimated probing depth, normalized to their respective maximum value for control and target samples. The intensity of the surface species is approximately the same for the probed depth. (d) Relative variation in pseudo-cubic unit cell parameters as a function of probing depth. Values were calculated from radial profiles of reciprocal space maps and averaged over several measurements on two sets of samples. The GIWAXS probing depth was varied by adjusting the angle of incidence of the X-ray beam between 0.12° and 0.3° . The error in the probing depth (horizontal error bars) was estimated from the angular error due to the surface roughness of the sample. The vertical error bars were determined from the standard deviation from repeated measurements on two sets of samples. Image taken from publication [II].

erated crystal structure of the crown ether complex based on previously reported crystal structures of crown ethers⁴⁰¹ showed that it is indeed expected to exhibit a diffraction signal around $0.5 \text{ \AA}^{-1}$. Therefore, the observed signals can be attributed to crystallites of the crown ether complex on the surface of the treated sample. The other signals at slightly lower q -values are consequently tentatively attributed to slightly different polymorphs of the crown ether crystal structure, which are known to occur.³⁹⁸ The broad signal in the

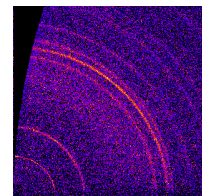


powder diffraction pattern is an additional hint towards structural variability and the tendency to form slightly differing polymorphs.

Varying the GIWAXS incidence angle and thus the surface sensitivity, allowed to determine the structural properties of the thin film as a function of probing depth, reflecting the gradient nature of the cation mixing. Analyzing the signal intensities from different crystal phases (Figure 9.9 (b)), it can be seen that in the control sample the signal intensity of the perovskite phase is nearly constant for all probing depths, which is as expected since the film consists mainly of perovskite material. In the target Cs^+ -doped sample, the relative intensity of the perovskite signal increases with probing depth, indicating a lower perovskite content on the surface, which contains the crown ether based surface species as well. This surface species is found to be indeed located exclusively on the film surface, as indicated by no relative intensity increase with higher probing depth, implying all of the material is already probed at lower depths. X-ray reflectometry (Figure D.8 (c), appendix) yields an estimated minimum thickness of the surface layer consisting of crown ether crystallites of approximately 15 nm.

Regarding the impurity phases, PbI_2 is not only present to a much higher proportion in the control sample than in the sample treated with the crown ether complex (compare Figures D.8 (a) and (b) in the appendix), but there is found considerably more of it on the film surface of the control sample relative to the perovskite phase as well. In the treated sample, the small amount of PbI_2 that is present in the material is distributed much more homogeneously throughout the film as indicated by a similar trend in signal intensity for both phases as a function of probing depth. This suggests that the surface treatment specifically reduced the excess PbI_2 phase at the film surface, which can be ascribed to protection of the surface against perovskite degradation.

Similar to PbI_2 , the $4\text{H}^{89,90}$ hexagonal polytype of FAPbI_3 can be found preferentially on the surface of the control sample. Since this phase is an intermediate stage between the perovskite α -phase and the non-photoactive δ -phase of FAPbI_3 , it could be either a sign of material degradation or it could be a residue of incomplete conversion during material fabrication. In any case it likely poses a risk toward further degradation. Therefore, the absence of 4H phase at the cesium-rich surface of the treated samples is another benefit of cesium cation infusion. The relative energies of 4H polytype and perovskite α -phase were calculated as a function of cesium cation concentration (detailed in publication [II]), which revealed that Cs^+ -doping significantly decreases the stability of the 4H polymorph relative to the α -phase. This is another instance of the beneficial effect of mixing cesium cations into FAPbI_3 -based perovskite materials, which is already observed in Section 9.1. The relative unit cell size of the perovskite phase as a function of probing depth, deter-

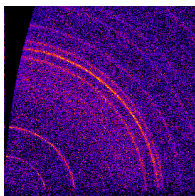


CHAPTER 9. COMPONENT MIXING

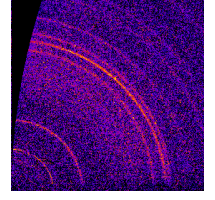
mined from the positions of the diffraction peaks, is displayed in Figure 9.9 (d). Therein it can be seen that both samples, including the control sample, exhibit a slightly smaller unit cell on the surface of the film, which is likely due to surface strain. However, the reduction in unit cell size is significantly more pronounced in the cesium-infused sample, as is expected for an inclusion of the smaller cesium cation into a FAPbI_3 perovskite structure. A gradual increase of the unit cell parameter with higher probing depths indicates a gradient in cesium concentration. Since a decreased unit cell size leads to an increase of the band gap, this size variation correlates to the formation of a wider-band gap cesium-substituted perovskite at the interface between the bulk perovskite and the hole transporting material. This could benefit the hole extraction and inhibit charge carrier recombination.

To further confirm and investigate the inclusion of cesium cations into the perovskite structure, solid state nuclear magnetic resonance (NMR) spectroscopy was employed, which is described in detail in publication [II]. Strong indications for a transfer of the cesium cations from the crown ether complex and inclusion into the perovskite structure could be found, corroborating the results from the X-ray investigations.

Photovoltaic Performance and Device Physics The photovoltaic performance of the perovskite thin films was investigated in a conventional solar cell configuration as described in publication [II], where experimental details on device fabrication and analysis can be found. The dibenzo-21-crown-7-CsI target treatment is compared with undoped control samples, homogeneously Cs^+ -doped samples and dibenzo-21-crown-7 treated samples. Figure D.10 (appendix) summarizes the photovoltaic performance parameters of differently treated perovskite thin films, clearly showing an improvement in all parameters with the target dibenzo-21-crown-7-CsI treatment. Homogeneous Cs^+ -doping improves the photovoltaic parameters by a much smaller amount, which is even surpassed by the influence of pure crown ether treatment, showing the beneficial influence of the crown ether at the perovskite film surface. Thus, the improvement of photovoltaic performance is a synergistic effect of the cation gradient structure and surface modulation by the crown ether through a multimodal host-guest complexation approach benefiting both bulk and surface properties. A more detailed discussion about the photovoltaic parameters and their variation upon treatment can be found in publication [II], as well as stability and lead leakage data, showing a beneficial effect of the surface treatment on both.



Conclusions This study showcases the multimodal approach of host-guest complexation to modify the surface of perovskite thin films. The beneficial effects include not only modification of the perovskite material itself by gradient doping, but likewise surface protective effects of the residual crown ether on the surface. Photovoltaic performance, material and operational stability as well as potential toxicity experienced improvement by treatment of a FAPbI_3 thin film surface with the dibenzo-21-crown-7- CsI complex. X-ray diffraction methods were applied among various further methods in this study, demonstrating its compatibility and complementary usage with those. In combination, a thorough characterization of structural, optoelectrical, molecular and photovoltaic material properties could be realized. GIWAXS analysis was a valuable tool in this collection of methods to elucidate the influence of cesium cation infusion on the phase composition of the material, new crystalline phases, as well as structural properties of surface and bulk, confirming a gradient doping profile.



9.3 Increase of Non-Perovskite FAPbI_3 Phase by Imidazolium Inclusion

In the previous two sections, adding alkali metal cations to the mixture for the central cation position is shown to stabilize and favor the formation of the formamidinium lead iodide (FAPbI_3) perovskite α -phase against the non-perovskite δ -phase. However, the opposite effect of inducing the growth of hexagonal δ -phase can be observed for certain mixing components as well, which is detrimental for material stability and photovoltaic performance. Thus, mixing these into FAPbI_3 -based materials may not be promotive to the material quality. One of these components is the imidazolium cation, the structure of which is shown in Figure 9.10 (f).

Although imidazolium has been found to be miscible with methylammonium for occupying the central cation position within a MAPbI_3 framework,⁴⁰² an analogous ImPbI_3 (where Im represents imidazolium) perovskite type of structure has not been observed so

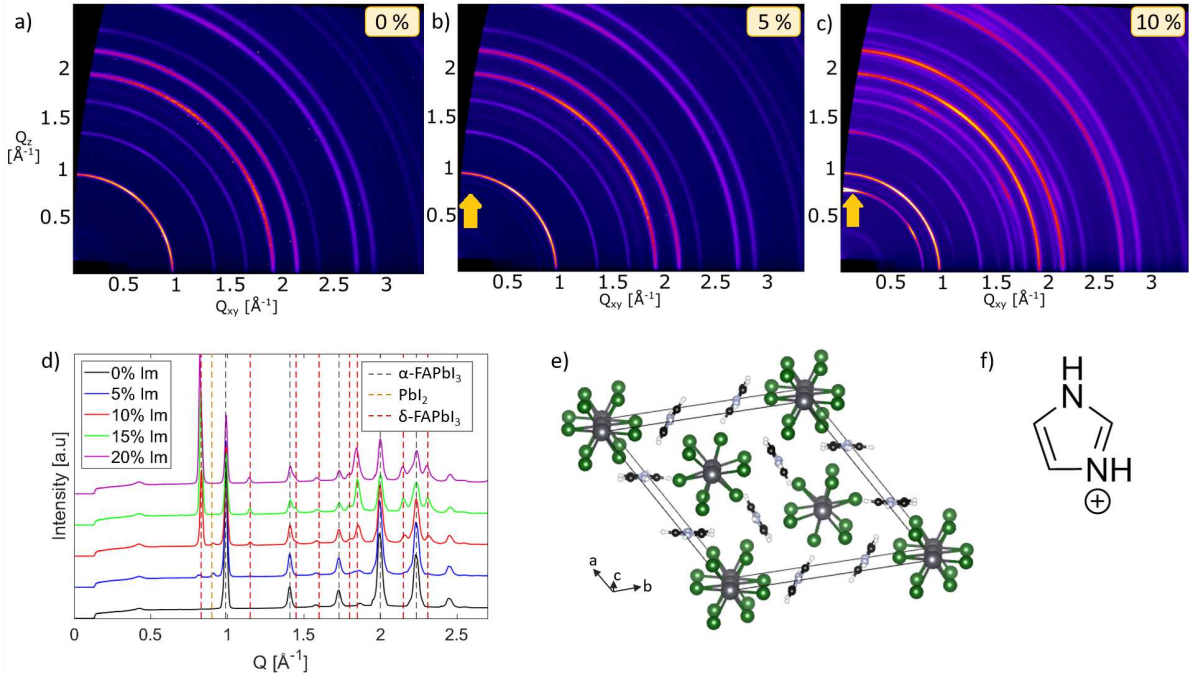
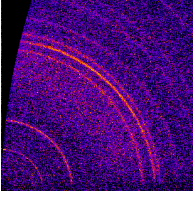


Figure 9.10: GIWAXS reciprocal space maps of (a) the $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ reference sample, (b) addition of 5 % and (c) 10 % of imidazolium. Data for higher imidazolium concentrations can be found in Figure D.11 (appendix). (d) Radial profiles of reciprocal space maps in (a) – (c) and Figure D.11. (e) Hexagonal crystal structure of ImPbI_3 (where Im represents imidazolium),⁹² showing similarities to the $\delta\text{-FAPbI}_3$ structure (Figure 2.8). (f) Molecular structure of imidazolium.



9.3. IMIDAZOLIUM INCLUSION

far.^{403,404} Instead, the compound ImPbI_3 has been reported to form a hexagonal structure⁹³ with 1D chain-like connected lead iodide octahedra.⁹² The structure is shown in Figure 9.10 (e), where the similarities to the hexagonal FAPbI_3 δ -phase (compare Figure 2.8) are apparent.

Thin films of $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ (denoted as $(\text{FA,Cs})\text{PbI}_3$) were fabricated with a similar procedure as reported in publication [I]. Different amounts of imidazolium were added to the precursor solution: 0 % (reference), 5 %, 10 %, 15 %, 20 % of the amount of total perovskite material. The reciprocal space maps in Figure 9.10 (a)–(c) show an increase of δ -phase intensity (signal marked with yellow arrows) with increasing imidazolium concentration. This is particularly visible in the radial profiles (Figure 9.10 (d)) by a strong increase of the δ -phase peak relative to the perovskite signal for imidazolium concentrations above 5 %. Additionally, a small amount of excess lead iodide can be observed with low imidazolium concentrations (5–10 %), but not for the higher concentrations nor the film without imidazolium.

In the in-plane intensity profiles (Figure 9.11 (a)), separate peaks of hexagonal FAPbI_3 and ImPbI_3 can be observed clearly only for thin films with 5 % imidazolium. For higher concentrations, the ImPbI_3 peak is merely a shoulder on an enhanced FAPbI_3 hexagonal phase peak. In the radial profiles (Figure 9.11 (b)), obtained from the reciprocal space maps, no separate peaks for ImPbI_3 and FAPbI_3 hexagonal phases can be seen for imidazolium concentrations above 10 %. Instead, a continuous shift of the FAPbI_3 peak positions to lower q with increasing concentration can be observed, indicating its move-

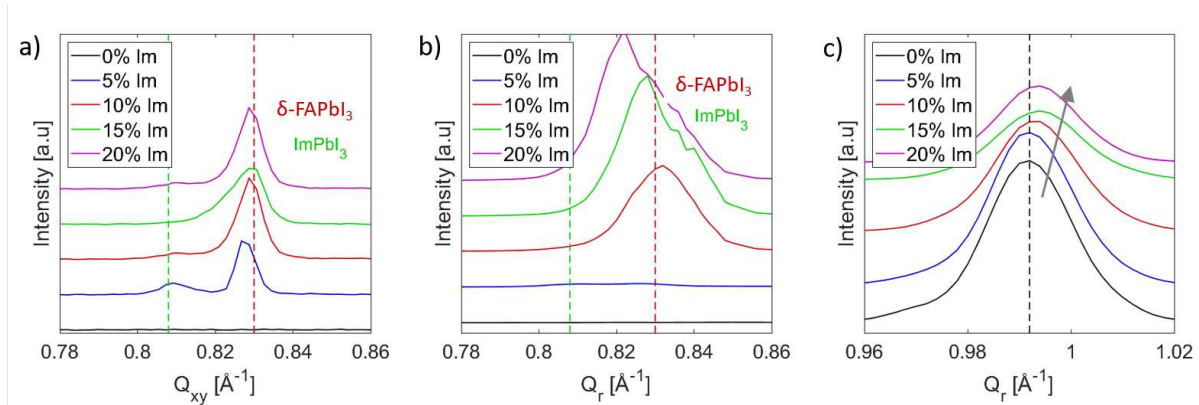
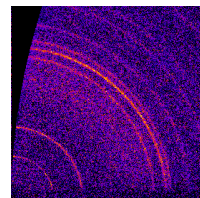


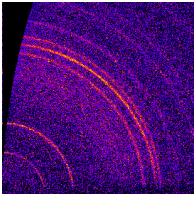
Figure 9.11: Enlarged sections of the δ -phase peak in (a) in-plane direction and (b) radial profile of the reciprocal space maps. (c) Close up of the α - FAPbI_3 (100) signal. The vertical dashed line marks the peak position of the reference material without imidazolium, while the gray arrow indicates a peak shift to higher q with increasing imidazolium concentration. In the legend, Im is short for imidazolium.



ment toward the ImPbI_3 position. Only in the sample with the lowest concentration (5 % imidazolium), a peak separation of the weak $\delta\text{-FAPbI}_3$ and ImPbI_3 signals can be noticed. Thus, it can be concluded that the addition of imidazolium to $(\text{FA,Cs})\text{PbI}_3$ perovskite induces the formation of hexagonal and lead iodide phases. The behavior differs between low (5 %) and high (≥ 10 %) concentrations of imidazolium. At low concentrations, the amount of PbI_2 phase is significantly increased, while separate hexagonal phases of ImPbI_3 and FAPbI_3 can be observed. The lattice parameter of the remaining $(\text{FA,Cs})\text{PbI}_3$ perovskite phase is not altered. This suggests a phase separation with a separate hexagonal ImPbI_3 phase. This hexagonal phase, however, potentially templates the growth of hexagonal $\delta\text{-FAPbI}_3$ and even hexagonal PbI_2 .

For higher imidazolium concentrations, at least part of the imidazolium is mixed into the hexagonal $\delta\text{-FAPbI}_3$. This is suggested by a reduction of the ImPbI_3 signal, which then only appears as a shoulder on a greatly enhanced FAPbI_3 signal. The increasing amount of FAPbI_3 δ -phase manifests in a reduction of the lattice parameter of the remaining perovskite phase as well, indicated by a shift of perovskite diffraction signals to higher q (Figure 9.11 (c)). This peak shift is considered to be caused by a reduction of the formamidinium ratio relative to the smaller cesium cation, and therefore reduction of the unit cell size. The signal of $\delta\text{-FAPbI}_3$ in the radial profiles shifts to lower q with increasing amount of ImPbI_3 from 10 – 20 %. This is consistent with an incorporation of the larger imidazolium cation into the hexagonal $\delta\text{-FAPbI}_3$ phase or at least a nanoscale mixing of the two hexagonal structures. This peak shift, however is not observed in the in-plane direction, indicating for an anisotropic expansion of the unit cell.

Conclusions It has been shown by this GIWAXS study that imidazolium does not mix into the $(\text{FA,Cs})\text{PbI}_3$ perovskite structure, but, if at all, into the hexagonal FAPbI_3 δ -phase, which is greatly enhanced upon imidazolium addition. Imidazolium, which is known to form a hexagonal ImPbI_3 structure in perovskite compositions, is observed to induce the formation of hexagonal $\delta\text{-FAPbI}_3$. For low imidazolium concentrations, separate ImPbI_3 and FAPbI_3 phases can be found. Possibly the amount of $\delta\text{-FAPbI}_3$ is not sufficient in these cases for all of the imidazolium to mix into it. With higher concentrations of imidazolium, the amount of $\delta\text{-FAPbI}_3$ is enhanced and the imidazolium can be mixed into the hexagonal FAPbI_3 to replace FA^+ . Thus, for obtaining and stabilizing a cubic perovskite phase, mixing imidazolium into $(\text{FA,Cs})\text{PbI}_3$ is not a favorable approach.



9.4 Halide Segregated Crystallization of Mixed Halide Perovskites

While the previous sections focus on substitution and mixing of the central cation, this section presents in-situ GIWAXS studies on mixed halide perovskites of the composition $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ where x ranges from 0 to 1. The concept of halide mixing, its potential benefits as well as resulting challenges such as halide segregation are introduced in Section 3.3. The work presented in this section is based on publication [III], including the investigation of halide segregation during light exposure, as well as tracking of the crystallization from the precursor solution to the final film during the fabrication process. A tendency to segregate is consistent with the distinct growth behavior of mixed halide thin films, where the crystallization pathways are observed to be different for iodide and bromide-rich phases. This leads to phase segregated growth and formation of a mixed halide perovskite only during thermal annealing. A bromide perovskite phase crystallizes first, already during spin-coating. The iodide fraction is converted only upon sample annealing via a solvent complex as an intermediate stage, and then intermixes into the bromide-rich perovskite phase. This behavior of separate crystallization sequences and intermixing of halides only upon heat treatment is consistently observed for different thin film fabrication protocols, including nitrogen gas-quenching and the lead acetate route.

Table 9.2: Final bromide fractions of segregated phases together with the fraction of the total material occupied by the respective phase. The bottom line gives the total bromide content of the sample as calculated from the determined phase mixtures. Values were obtained by fitting the split diffraction peaks with multiple Gaussians.

Nominal bromide content	80 %	60 %	40 %
Bromide content segregated phase 1	57 %	33 %	20 %
Fraction phase 1 (of total material)	54 %	55 %	54 %
Bromide content segregated phase 2	94 %	88 %	57 %
Fraction phase 2 (of total material)	46 %	45 %	46 %
Calculated total bromide content	74 %	57 %	37 %

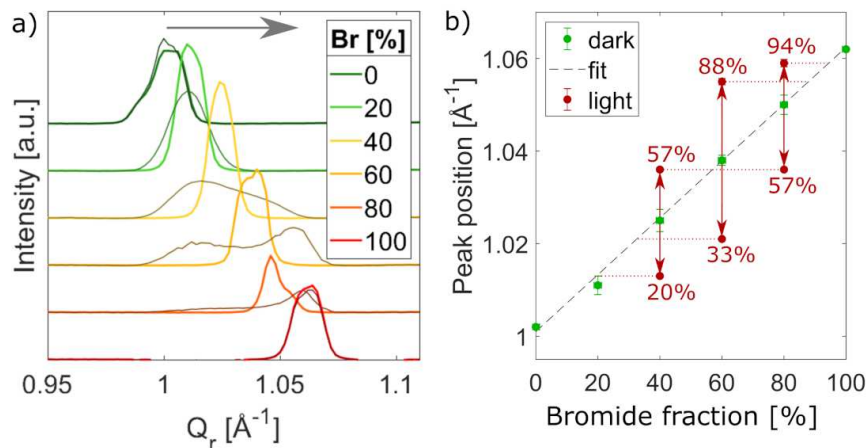
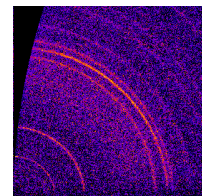
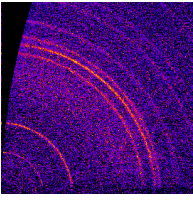


Figure 9.12: (a) Enlarged section of the radial profiles of GIWAXS reciprocal space maps (incidence angle $\alpha_i = 1^\circ$) of $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ thin films, highlighting the (100) perovskite diffraction signal. Brightly colored, thicker lines: fresh samples in the dark; faded, thinner lines: after illumination and phase segregation. (b) Fitted peak positions of the data in (a) with a linear fit following Vegard’s law.¹⁸⁶ Red numbers in (b) indicate final bromide fractions of segregated phases after light exposure as determined from assuming a linear dependency (horizontal red lines), which are displayed in detail in Table 9.2. Image taken from publication [III].

Mixing Behavior and Phase Segregation Mixed halide perovskite thin films of the composition range $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ were prepared by spin-coating, including two different fabrication routes, the lead acetate route⁴⁰⁵ and the gas quenching technique²⁸⁰ with a nitrogen flow (details in the experimental section of publication [III]). For the bromide ratio x , six values were chosen: 0, 0.2, 0.4, 0.6, 0.8 and 1, with 0 and 1 marking the pure iodide and pure bromide perovskites, respectively. Both methods yield similar results in the final films (compare Figures D.12 and D.13 (a), appendix): In the absence of light, the thin films exhibit a single mixed perovskite phase, which appears to contain a macroscopically homogeneous mixture of halides.

As reported previously,³⁶ an expected peak shift of the perovskite diffraction signal is observed with changing mixing ratio of bromide and iodide (Figure 9.12 (a)). The peak position shifts linearly with the halide ratio, following Vegard’s law for binary mixtures.¹⁸⁶ For the measurement in the dark, most mixed compositions feature a single, yet rather broad peak, indicative of a single mixed halide phase. Only the mixture with the highest bromide content (80 %) shows a shoulder towards higher q , which indicates an already



beginning phase segregation. The double peak observed for MAPbI_3 is due to its tetragonal structure, while all further mixtures exhibit a cubic symmetry.³⁶

Upon illumination with a halogen lamp, peak splitting is observed for all mixed materials except the one with 20 % bromide, where a pronounced peak broadening can be found instead (faded lines in Figure 9.12 (a)). The single halide materials do not exhibit significant modifications of the diffraction pattern upon illumination, indicating a negligible thermal expansion effect. The light-induced peak splitting in the mixed materials is characteristic for a segregation into iodide and bromide-rich phases,¹⁹⁰ while the broadening of the signal in the 20 % bromide sample at least shows an increase in disorder or a wider variety in unit cell parameter throughout the sample as a result of illumination. This could be attributed to close-lying overlapping diffraction signals indicating a separation into phases of maximum $\pm 4\%$ bromide content deviation, as determined from converting the peak position spread into concentration.

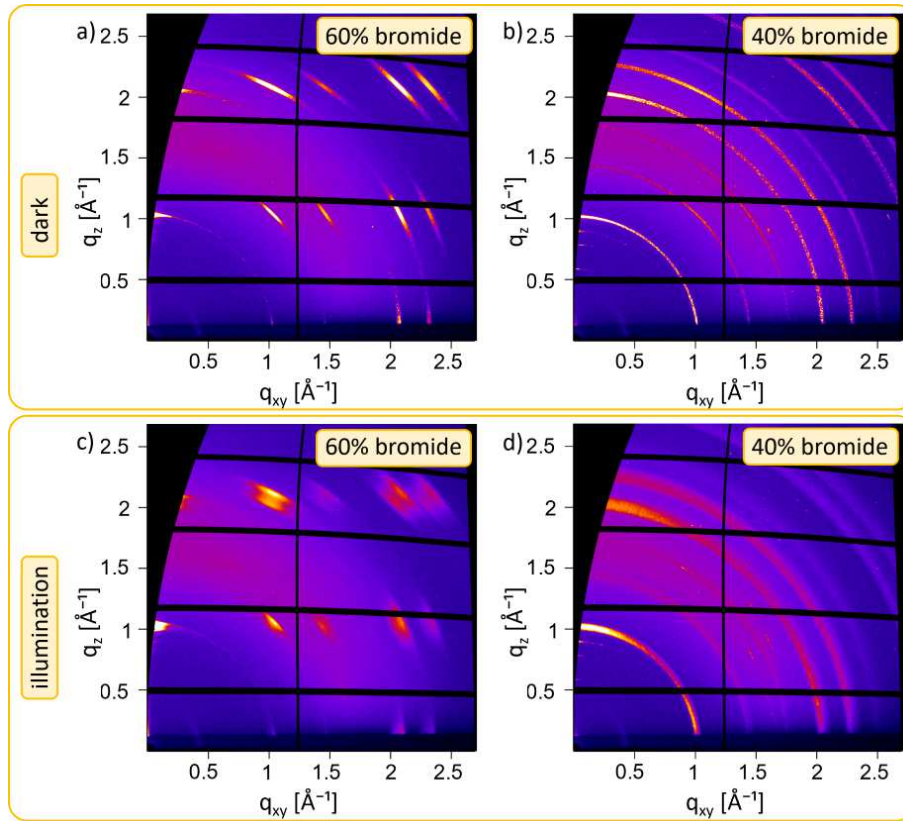
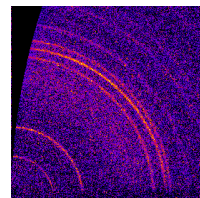


Figure 9.13: GIWAXS reciprocal space maps (a), (b) before and (c), (d) after illumination of $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ thin films with (a), (c) 60 % and (b), (d) 40 % of bromide content. A clear peak splitting can be observed after illumination, while the orientational order is retained. Image taken from publication [III].

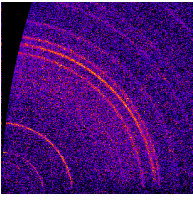


Determining the positions of the split peaks after illumination, Vegard's law can be used to calculate the final compositions of the segregated phases, as indicated by the red horizontal dashed lines in Figure 9.12 (b). The resulting values for each segregated composition are represented by the red numbers in the image and in Table 9.2. Considering the final compositions and assuming a steady state was reached as suggested by the temporal evolution of the peak positions (Figure D.15, appendix), the system appears to separate until one of the two main segregated phases either exhibits a low bromide content of $\leq 20\%$ or a high bromide content of $\gtrsim 90\%$, which is consistent with previous reports.²⁰³ It should be noted, though, that the strong illumination likely increased the temperature of the sample as well, and thus entropic contributions, which tend to favor mixing,^{195, 205, 223, 225} potentially inhibited a full segregation into pure-halide phases. This is considered to contribute to the distinct broadening of the diffraction signals as well, indicating not only two segregated phases with the distinct compositions given, but possibly a distribution of mixed phases with a continuum of mixing ratios beside the two majority phases.

By comparing reciprocal space maps of thin films with different mixing ratios before and after illumination (Figure 9.13, more mixing ratios in Figure D.13, appendix), it is apparent that the degree of orientation is determined by the mixing ratio. Higher bromide mixtures exhibit an increased degree of orientational order along the vertical axis, as indicated by spot-like diffraction signals in the respective reciprocal space maps as opposed for ring-like features for more randomly oriented iodide-rich compositions. This finding is generally true for both gas quenching and lead acetate-based fabrication protocols, while the gas-quenching method overall produces thin films with a slightly higher orientational order (compare Figures D.12 and D.13 as well as Figure D.14 for azimuthal angular profiles). Increasing orientational order of methylammonium-based perovskite materials upon bromide incorporation likely is a general motif, which has been reported in literature before.⁴⁰⁶

The degree of orientation is not altered upon halide segregation, such that both split peaks possess the same orientation as the pristine samples. This behavior is consistent with halide segregation occurring via ion migration in the existing perovskite crystallites instead of re-crystallization or via amorphous phases.

For the time scale of the segregation with the present setup, 10 – 15 minutes were enough to reach a stable state in which the diffraction pattern did not visibly change anymore. Demixing was monitored by real time GIWAXS (Figure D.15, appendix, details in the experimental section of publication [III]) and observed to take place gradually, indicated by two closer lying diffraction peaks in the early stages of illumination, which move further apart until the final positions corresponding to the final segregated phase compositions



are reached. Variation of the X-ray incidence angle (Figure D.16, appendix) reveals that the bromide-rich phase is observed to be located predominantly in vicinity of the surface of the sample, while consequently the iodide-rich phase should be farther away from the surface, i.e. closer to the bottom of the thin film.

These findings are consistent with current literature,^{203,407} yet critical hints why mixed halide perovskite thin films behave this way are expected to be found already in their fabrication and crystallization pathway. Thus, the following two paragraphs elucidate on the perovskite phase formation during two different thin film fabrication protocols, featuring first the rather simple gas quenching technique, followed by the slightly more sophisticated lead acetate route. Details on fabrication procedures can be found in the experimental section of publication [III].

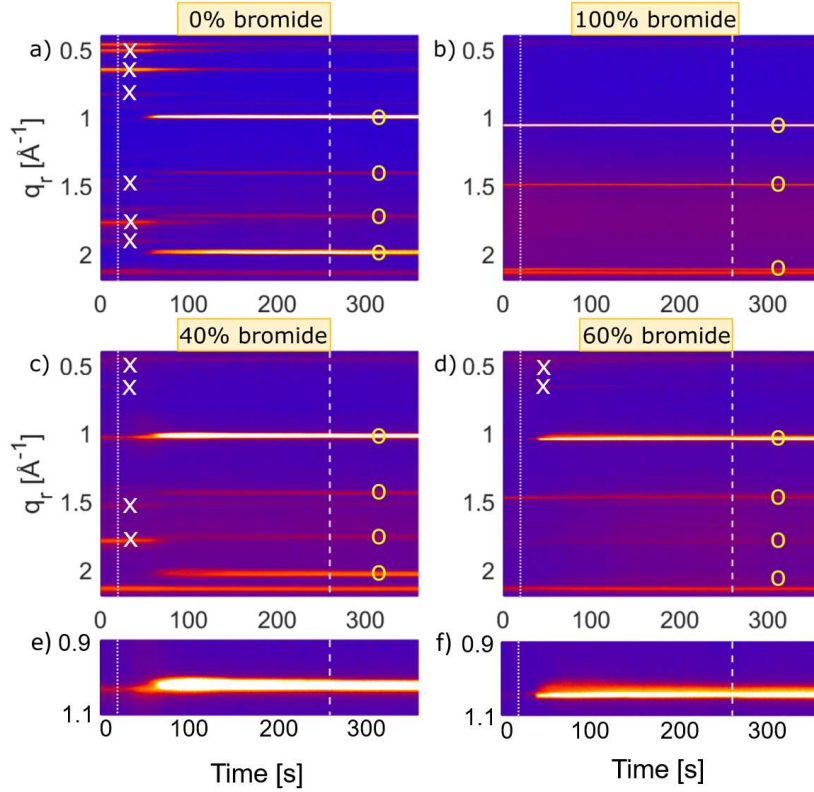
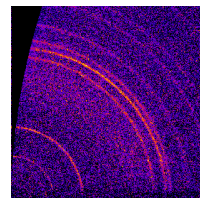


Figure 9.14: Intensity maps from radial profiles of GIWAXS reciprocal space maps as a function of time during thermal annealing for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ samples fabricated via the N_2 gas quenching route. (a) 0 % bromide/pure MAPbI_3 , (b) 100 % bromide, (c) 40 % bromide, (d) 60 % bromide. White crosses mark the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ phase, while perovskite phase is marked with yellow circles. (e), (f) Close ups of the region around $q = 1 \text{ \AA}^{-1}$ in (c), (d). Vertical white dotted lines: start of heating; dashed lines: heat source turned off. More mixing ratios can be found in Figure D.17 in the appendix. Image taken from publication [III].



Thin Film Crystallization via Nitrogen Gas Quenching In-situ GIWAXS was employed to investigate the thin film growth and crystallization in real time to connect these processes to the mixing and segregation behavior. GIWAXS was recorded during the spin-coating as well as the annealing process of the mixed halide thin films for both fabrication routes. The findings via the gas quenching route are discussed first, due to the simplicity of the process omitting influences such as antisolvents, additives or unequal stoichiometries on the film growth. Afterwards they are compared to the results of the slightly more complex lead acetate route, which achieves similar final films, but via different crystallization sequences.

For the gas quenching route, the pure MAPbI_3 composition initially forms the solvent complex $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ during spin-coating,¹⁰² marked by white crosses in Figure 9.14 (a), which shows the evolution of the radial intensities of the reciprocal space maps during the film formation process. The corresponding integrated peak intensities of signature peaks in Figure 9.15 (a) and (e) show that thermal annealing converts the intermediate solvent complex to the perovskite phase, which is marked by yellow circles in Figure 9.14. Conversely, the pure MAPbBr_3 composition (Figures 9.14 (b) and 9.15 (d), (h)) directly crystallizes in the perovskite phase and does not change significantly during annealing. For mixed films, the distinct signals of the bromide-based perovskite structure already appear during spin-coating as well (Figure 9.15 (b), (c) and D.18, appendix). From the peak position, this is considered to be an almost pure bromide perovskite (Figure D.20, appendix). An increasing iodide fraction within the composition results in stronger scattering signals of the solvent complex $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$, which evolve during the annealing (Figures 9.14 (c), (d) and 9.15 (b), (f), (g)). With low iodide content ($\geq 60\%$ bromide), the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ phase is not observed during the spin-coating, but only temporarily in minor amounts during thermal treatment (compare also Figures D.18, D.17 and D.19, appendix). In the course of the annealing procedure, the signals of the solvent complex phase vanish, together with a shift of the perovskite peaks towards lower q -values, indicating an increase of the unit cell size, which reflects inclusion of the larger iodide ions into the perovskite structure (Figure D.20, appendix). A similar type of sequential crystallization with changing halide composition has been reported before for all-inorganic perovskite structures.⁴⁰⁸

Additionally, for the mixed compositions, the perovskite peaks not only shift upon annealing, but widen as well, especially in early stages of annealing, indicative of an increased amount of disorder, which reflects a smaller domain size or slight differences in unit cell size throughout the sample (Figure D.21, appendix). In addition, the peak broadening might be related to a partial dissolution of the bromide-rich domains upon the start of

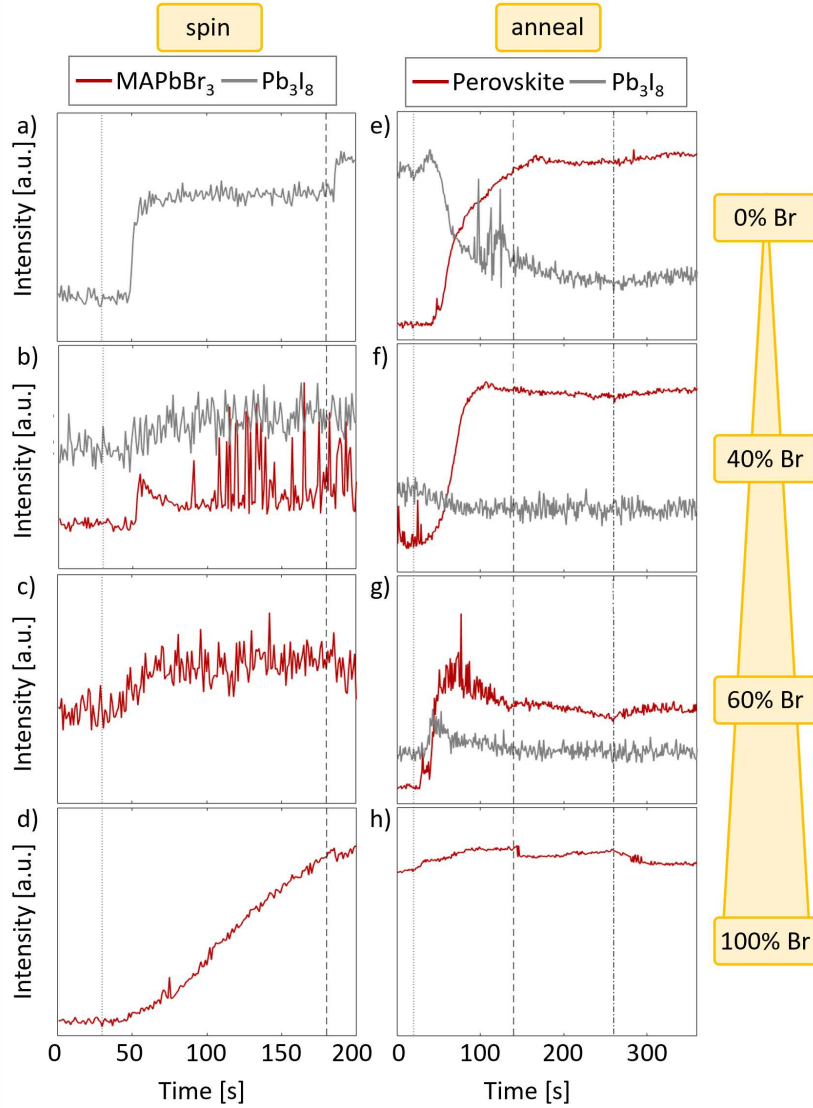
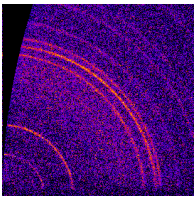
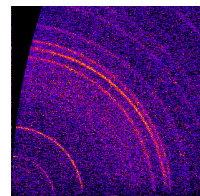


Figure 9.15: Normalized integrated peak intensities from radial profiles as a function of time during (a) – (d) spin-coating and (e) – (h) annealing for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ samples fabricated via the N_2 gas quenching route. (a), (e) 0 % bromide/pure MAPbI_3 , (b), (f) 40 % bromide, (c), (g) 60 % bromide, (d), (h) 100 % bromide. Legend colors apply for all samples, except during spin-coating the red curve marks the bromide-rich perovskite phase and in the annealing data the mixed perovskite phase. A list of the signature peaks used for all phases can be found in Table D.1 in the appendix. Vertical dotted lines in (a) – (d): start of spinning; dashed lines: end of spinning. Vertical dotted lines in (e) – (h): start of heating; dashed lines: reduction of heating power; dot-dashed lines: heat source turned off. Pb_3I_8 in this case is short for the DMSO-based $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ solvent complex. More mixing ratios can be found in Figure D.19 in the appendix. Image taken from publication [III].



iodide intermixing. During prolonged annealing, the peak width is reduced again, suggesting a more even mixing of halides with a more uniform distribution of unit cell sizes. This can be seen clearly in the close ups of the profile evolution of the perovskite (100) signal in Figure 9.14 (e) and (f), where an initial higher- q peak is followed by a broader peak shifted to lower q , indicating the increase of unit cell size upon iodide inclusion as well as an increase of disorder in early stages of mixed perovskite formation, likely including a smaller coherent domain size.

A direct crystallization of MAPbBr₃ perovskite without intermediate stages or even need for annealing has been observed before and is ascribed to the higher bonding strength between Pb²⁺ and Br⁻ compared to the I⁻ ion⁴⁰⁹ or a reduced stability of the lead bromide solvent adducts.⁴¹⁰ For the iodide compound MAPbI₃, the growth via intermediate solvent complexes is well reported.^{102,105,108–110,112,123} Interestingly, for the mixed halide samples, both processes, direct MAPbBr₃ crystallization and MAPbI₃ formation via intermediates were observed simultaneously, leading to initial growth of a bromide-rich perovskite phase and subsequent intermixing and inclusion of iodide after thermal conversion of the iodide-based solvent complex.

Thin Film Crystallization via the Lead Acetate Route The above investigations were done for thin films fabricated by nitrogen gas quenching, which is now compared to the lead acetate route. This method is often used to tune thin film microstructure⁴⁰⁵ and was applied in this study for fabrication of the samples subjected to light induced segregation described in the first paragraph of this section. The deposition process during this fabrication route was investigated in real time as well to assess the universality of the crystallization behavior over different fabrication protocols.

The overall crystallization behavior during the lead acetate route was generally similar to the nitrogen quenching: iodide and bromide-based phases followed their separate crystallization sequences in parallel and a mixed perovskite phase was formed only upon thermal annealing.

MAPbI₃ formed via a structurally similar solvent intermediate as for the gas quenching method, in this case DMF-based MA₂Pb₃I₈·2DMF¹⁸ since DMSO was absent in the precursor solutions for this fabrication route (Figures 9.17 (e) and D.22 (a), appendix). Due to the highly non-stoichiometric nature of the precursor solution with its 3:1 ratio of MA:Pb, hexagonal MAPbI₃ could be observed during spin-coating (Figures 9.16 (a) and 9.17 (a)), which has been reported to occur only with a large methylammonium and halide excess.¹⁵⁵ This hexagonal MAPbI₃ phase,¹⁵⁴ according to the positions of its diffraction

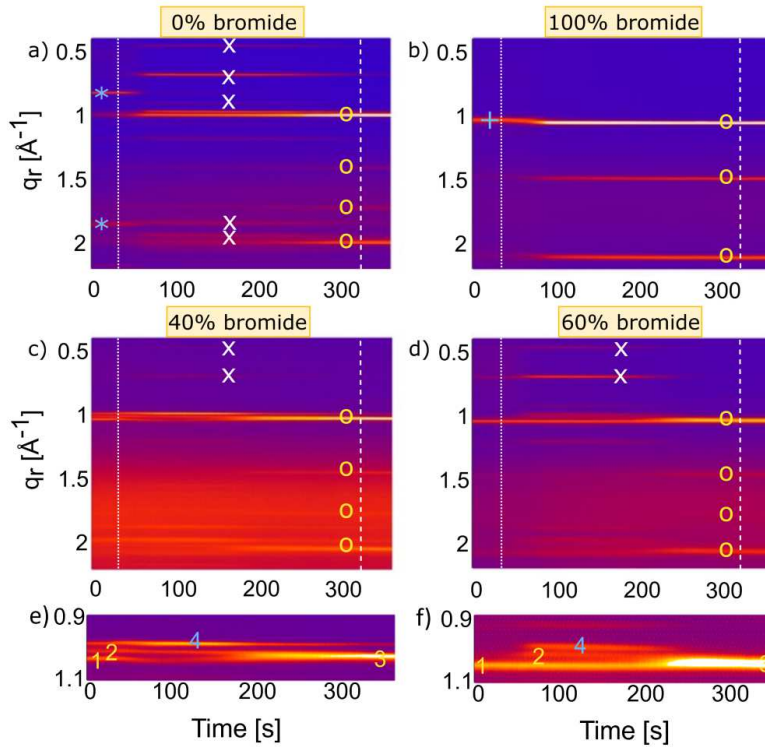
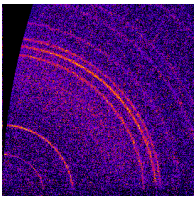


Figure 9.16: Intensity maps from radial profiles of GIWAXS reciprocal space maps as a function of time during thermal annealing for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ samples fabricated via the lead acetate route. (a) 0 % bromide/pure MAPbI_3 , (b) 100 % bromide, (c) 40 % bromide, (d) 60 % bromide. White crosses mark the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMF}$ phase, while perovskite is marked with yellow circles. Blue asterisks mark hexagonal MAPbI_3 in (a) and blue plus signs the layered MA_2PbBr_4 phase in (b). Vertical white dotted lines: start of heating; dashed lines: heat source turned off. (e), (f) Close ups of the region around $q = 1 \text{ \AA}^{-1}$ in (c), (d). Numbers in (e) and (f) indicate bromide-rich (1), iodide-rich (2) and mixed (3) perovskite phases and the layered MA_2PbBr_4 phase (4). Image taken from publication [III].

signals (blue asterisks in Figure 9.16 (a)), is assumed to exhibit a similar structure as the well-known FAPbI_3 δ -phase⁸⁹ containing linear chains of lead halide octahedra. Via a complex three-phase conversion sequence involving the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMF}$ solvent complex phase as well, a MAPbI_3 perovskite phase is established during prolonged thermal annealing (Figure 9.17 (e)).

Bromide perovskite, similarly to the gas quenching method, did not form crystalline solvent including intermediates (Figures 9.16 (b) and 9.17 (d), (h)). Nevertheless, upon deposition from the lead acetate-based solution, a crystalline precursor phase formed during spin-coating (marked by blue plus signs in Figures 9.16 (b) and D.22, appendix),

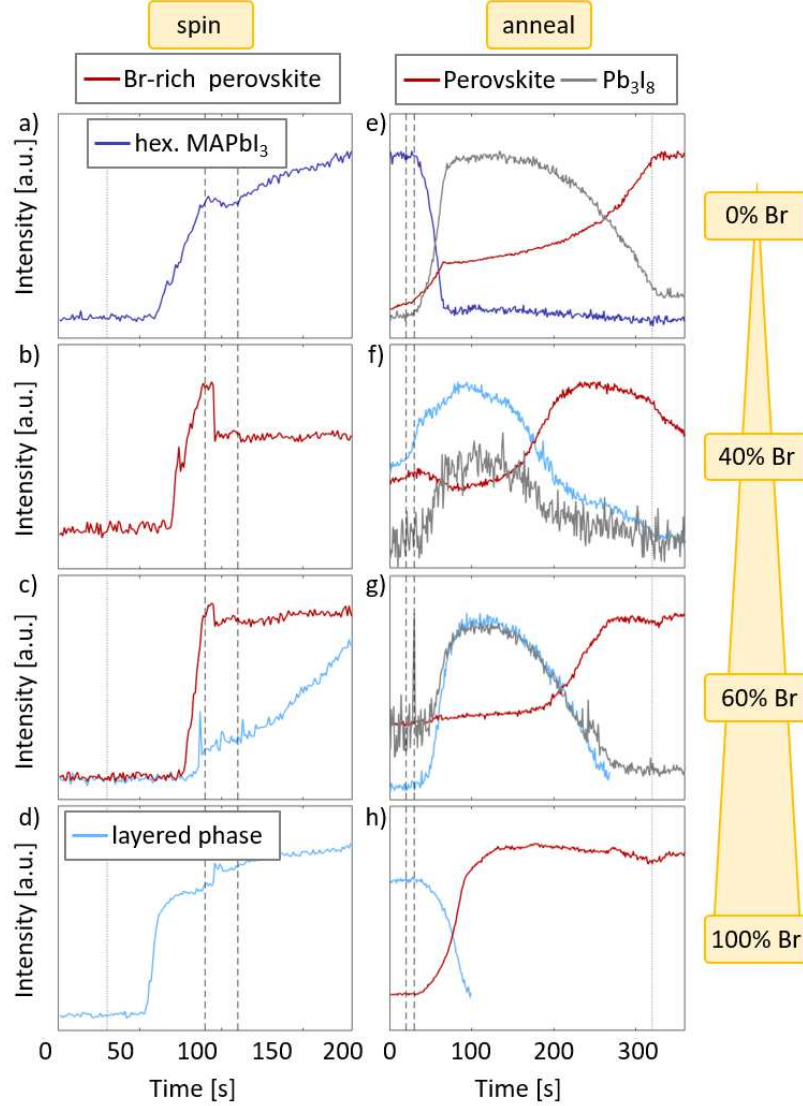
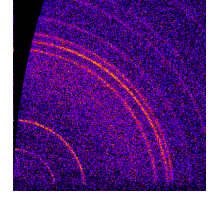


Figure 9.17: Normalized integrated peak intensities from radial profiles as a function of time during (a) – (d) spin-coating and (e) – (h) annealing for $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ samples fabricated via the lead acetate route. (a), (e) 0 % bromide/pure MAPbI_3 , (b), (f) 40 % bromide, (c), (g) 60 % bromide, (d), (h) 100 % bromide. Legend colors apply for all samples, except during spin-coating the red curve marks the bromide-rich perovskite phase and in the annealing data the mixed perovskite. A list of the signature peaks used for all phases can be found in Table D.1 in the appendix. Vertical dotted lines in (a) – (d): start of spinning; dashed lines: end of spinning/end of air flow. Vertical dashed lines in (e) – (h): start of heating/reduction of heating power; dotted lines: heat source turned off. Pb_3I_8 in this case is short for the DMF-based $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMF}$ solvent complex. Image taken from publication [III].

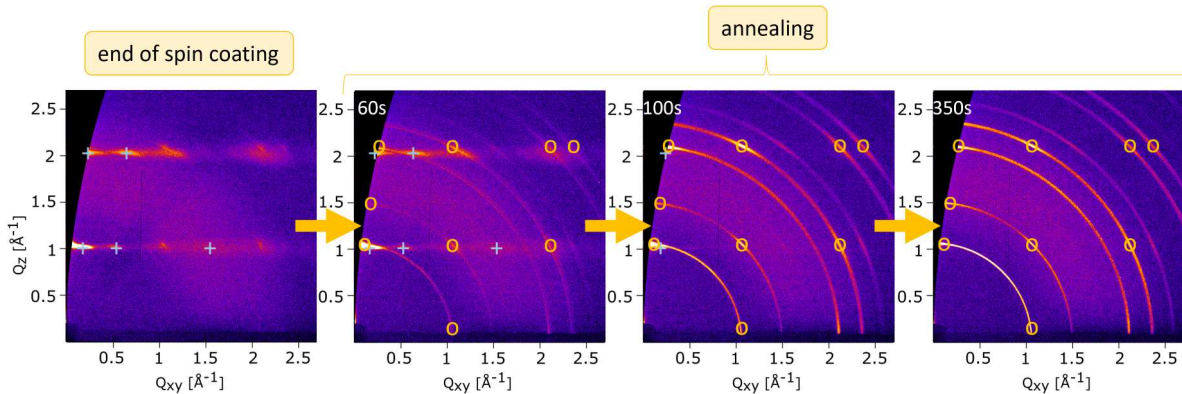
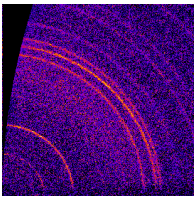
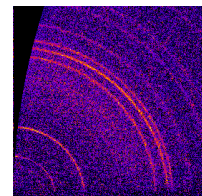


Figure 9.18: GIWAXS reciprocal space maps at selected time instances during deposition of MAPbBr_3 via the lead acetate route to illustrate conversion of the layered MA_2PbBr_4 phase into MAPbBr_3 perovskite. Blue plus signs mark the MA_2PbBr_4 structure, while yellow circles indicate MAPbBr_3 perovskite. Linear horizontal alignment of the signals for MA_2PbBr_4 reflects its well oriented layered nature. This likely templates a preferred orientation in the perovskite structure, indicated by angular intensity maxima in the ring-shaped diffraction features. Image taken from publication [III].

which was then transformed to the MAPbBr_3 perovskite structure during annealing. Due to its slightly lower q diffraction signal of around $1.038 \text{ \AA}^{-1}$, as compared to MAPbBr_3 ($q=1.06 \text{ \AA}^{-1}$),⁵³ which indicates a larger unit cell than the MAPbBr_3 perovskite, it is suspected to be a layered MA_2PbBr_4 phase. This kind of structure is only expected to form with a pronounced lead deficiency¹⁰⁶ in the precursor solution, which indeed was present here due to a 3-fold excess of MABr in the formulation. The formation of a layered intermediate phase is considered to be a hint towards the reason for the higher tendency of bromide-based compositions to form well-oriented perovskite phases. Their growth might be templated by locally formed nuclei of the layered phase, which are generally well-oriented. The conversion of this templating layered structure into perovskite is illustrated by reciprocal space maps at representative time instances in Figure 9.18.

Similarly to the gas quenching route, in the mixed samples, iodide and bromide-based phases evolve separately with and without solvent complex intermediates, respectively. Only at the later stages of annealing they merge into a single, macroscopically mixed perovskite phase. All mixed samples already exhibit a perovskite phase during spin-coating (Figure D.22, appendix), which according to its peak position of about $q = 1.06 \text{ \AA}^{-1}$ is a bromide-based perovskite phase.⁵³ During annealing, the layered MA_2PbBr_4 phase and the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMF}$ solvent complex evolve simultaneously and are transformed into the perovskite phase (Figures 9.16 (c)–(f) and 9.17 (f), (g)). Despite Figure



9.17 displaying the perovskite phase as a single graph, a close look to the diffraction peak and its development (Figure 9.16 (e), (f) and Figure D.23, appendix) reveals initially two close-lying peaks (marked by 1 and 2) corresponding to two separate bromide and iodide-rich perovskite phases, which merge into one significantly broader diffraction peak with an intermediate q -value (marked as 3). The signal of the layered phase (marked as 4) disappears simultaneously to this process, indicating its conversion to perovskite phase. Thus, the separate growth of iodide and bromide perovskite with subsequent halide mixing presents as a general pattern, which is retained over different fabrication routes.

Finally, the observed growth behavior is consistent with the properties of the final thin films: First, it offers an explanation for the dependence of orientational order on the bromide content since the bromide perovskite phase nucleates oriented growth, which is retained when intermixing iodide to a certain extent depending on the amount of bromide present. Second, the parallel crystallization sequences hint towards a segregation tendency of mixed iodide-bromide perovskites. This leads to a bromide-based perovskite matrix, established at room temperature, which is interspersed with iodide only upon annealing, resulting in a macroscopically uniform mixture, that likely still contains locally enriched regions of iodide or bromide.

Conclusions In summary, the detailed route of mixed halide perovskite thin film growth (simplified schematic depiction in Figure 9.19) was unraveled and connected to the mixing and segregation behavior. Literature reported phase segregation behavior could be repro-

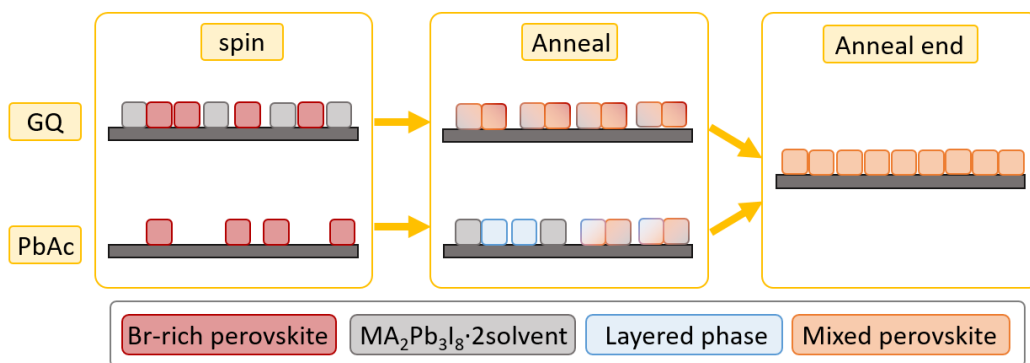
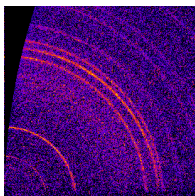
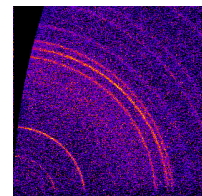


Figure 9.19: Schematic depiction of the crystallization behavior of mixed halide perovskite thin films. GQ: gas quenching; PbAc: lead acetate route. Bromide-rich perovskite phase forms already during spin-coating, while the iodide fraction forms intermediate crystalline solvent complexes based on DMF or DMSO. During annealing, the mixed halide perovskite phase is established. Image taken from publication [III].



duced and a gradual segregation into bromide and iodide-rich domains was found. The characteristic growth behavior of mixed halide perovskites was revealed, where in mixed compositions, bromide and iodide-based phases follow separate crystallization sequences and only form a mixed halide perovskite phase upon annealing. While the iodide-based fraction crystallizes via intermediate solvent complexes, these are not observed for the bromide fraction, which crystallizes directly as a perovskite phase and is interspersed with iodide during thermal treatment. Using highly non-stoichiometric precursor solutions like in the lead acetate route generates low dimensional phases as an intermediate stage, but the general motif of halide segregated crystallization sequences and formation of a mixed perovskite only upon thermal annealing is indicated to be universal.

This distinct growth behavior, which is retained even for different fabrication methods, offers a further piece in the puzzle of halide segregation, its causes and mechanisms. The fact that intermixing only happens during thermal treatment reflects the entropic contribution to halide mixing, but the intrinsic tendency to segregate manifests in a separate growth sequence for the bromide and iodide-based fractions of the material. This could in turn cause small inhomogeneities in the final film due to imperfect mixing, which could then serve as nucleation centers for halide segregation. The segregated growth process might thus be linked to potential seeds for light induced halide segregation. Therefore, future research might be dedicated to establishing fabrication methods for mixed halide perovskite thin films which promote halide mixing already during crystal growth and prevent segregated crystallization sequences.



9.5 Final Remarks on Mixed Perovskite Compositions

This chapter has presented the effects of mixing and adjusting the ions creating a perovskite structure. Special focus was on the central cation and the halides.

For the central cation, it was found that smaller cations, which can be included into FAPbI_3 based perovskite materials in limited amounts, generally stabilize the FAPbI_3 α -phase to quantitative amounts, achieving almost phase-pure α -phase perovskite. This holds for gradient structures as well, where only the surface is infused with cesium, providing a stabilizing effect but retaining the bulk FAPbI_3 properties. Cesium in general is a good alloy partner for formamidinium since CsPbI_3 and FAPbI_3 are well miscible in their α -phases, as well is MAPbI_3 . Including even smaller cations has shown to be challenging since rubidium inclusion cannot be completely proven, however a stabilizing effect of rubidium incorporation on α - FAPbI_3 is in any case observable.

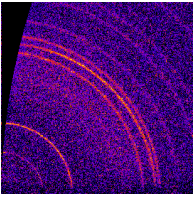
Including larger cations, such as imidazolium, even though with MAPbI_3 it is feasible, leads to an increased formation of non-perovskite phase in FAPbI_3 based compositions and is likely not promotive for perovskite formation.

For mixing the halide anions, although a general macroscopic miscibility is observed, gradual halide segregation occurs under light exposure. A tendency to segregate is already observed during the crystallization and growth process of mixed halide perovskite compositions, which crystallize in parallel sequences for each halide and only form the mixed phase upon thermal annealing.

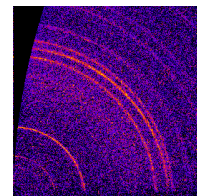
Thus, in this chapter, a quantification of the effects of mixing the central cation and halides was presented as well as the distinct effects of ion mixing and phase segregated growth.

The possible effects of phase stabilization or destabilization by various components is a key parameter to consider when designing materials. Similarly, phase segregation tendencies require consideration, including possible mitigation strategies to form the most stable perovskite material which does neither degrade into non-perovskite phases nor undergo phase segregation, since both can be detrimental to material properties relevant for device performance.

X-ray based techniques such as GIWAXS served as valuable tools among others to elucidate the structural characteristics of perovskite thin films during and after fabrication. Qualitative and quantitative as well as time-resolved structural information is obtained and correlated to results from further methods for a thorough investigation of structural variation as a function of composition and its effects on the material properties.



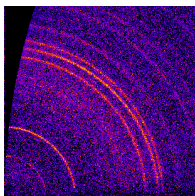
9.5. FINAL REMARKS



Chapter 10

Modifying Perovskite Thin Film Growth and Grain Morphology by Additives — The Example of Thiourea

Besides component mixing, the crystallization and therefore structure and morphology of perovskite thin films can be modified by many further process parameters, such as the precursor solvent composition, which dictates the type of intermediate structures formed, depending on the complexation abilities with the precursor materials.^{411–413} Precursor complexation is presumed to play a role with commonly applied additives, which do not incorporate into the crystal structure, but exert their distinct effects during the material fabrication.^{282,414,415} While the impact of solvent and additive engineering on perovskite grain structure is well reported, the underlying mechanisms that govern the crystallization process are still under debate.⁴¹⁶ Colloidal complex structures are presumed to be already present in perovskite precursor solutions, where the lead halide compound acts as an acceptor and the polar aprotic solvent molecules as donors in a Lewis acid-base type of interaction.^{122,276,277,416,417} Thus, an impact on the crystallization process is expected already by complexation and colloid formation in the precursor solution. The question how and during which fabrication step common additives such as thiourea influence the perovskite growth is covered in this chapter, as well as its influence on the precursor complexation in the perovskite ink, which is found to be remarkably limited. While Section 10.1 pinpoints the critical step for the impact of thiourea on the crystallization, Section 10.2 investigates its dependence on kinetics in more detail and finally Section 10.3 elucidates on the dependence on the perovskite composition.



10.1 Effects of Thiourea Addition on MAPbI₃ Thin Film Growth During the Full Fabrication Route

This section presents a comprehensive study including precursor chemistry, thin film deposition and the final thin film and device properties based on perovskite thin films with and without additives. In-situ GIWAXS provides the link between complexation in the precursor solution and the final product by elucidating the crystallization sequence and the exact moment when the chosen additive exerts its effect. The section is based on manuscript [i].

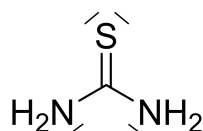


Figure 10.1: Molecular structure of thiourea.

Therein, the archetypal methylammonium lead iodide (MAPbI₃) was selected for the perovskite composition, together with the well-established solvents dimethylformamide (DMF), dimethylsulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP), including thiourea as an additive, which is reported as a Lewis-base additive with donor properties via its sulfur atom. Its molecular structure is shown in Figure 10.1. Addition of thiourea reportedly affords a notable increase of the grain size in perovskite thin films produced from a variety of different perovskite precursor ink compositions.^{281–284} Thiourea was chosen over other common additives, such as Pb(SCN)₂ or MACl, as it neither modifies the lead iodide ratio in the precursor ink, nor undergoes dissociation upon dissolving, which would add charged species that would immediately interfere with analysis.

Complex Formation in Solution To investigate complex formation in the perovskite precursor solution, ²⁰⁷Pb nuclear magnetic resonance (NMR) spectroscopy was conducted on precursor solutions in a relevant concentration regime of 0.1 – 1.5 mol/l, employing the solvents DMF, DMSO and NMP, all of which possess electron lone pairs that can act as a donor with relatively high donor numbers, quantifying the electron-donating ability, of 26.6 kcal/mol, 29.8 kcal/mol and 27.3 kcal/mol, respectively.^{419,420} The concentration was systematically varied in all solvents since it has shown to impact the complexes in highly diluted perovskite precursors,^{122,417} investigating solutions of pure PbI₂ or stoichiometric MAPbI₃. Due to fast chemical exchange among potential different iodoplumbate

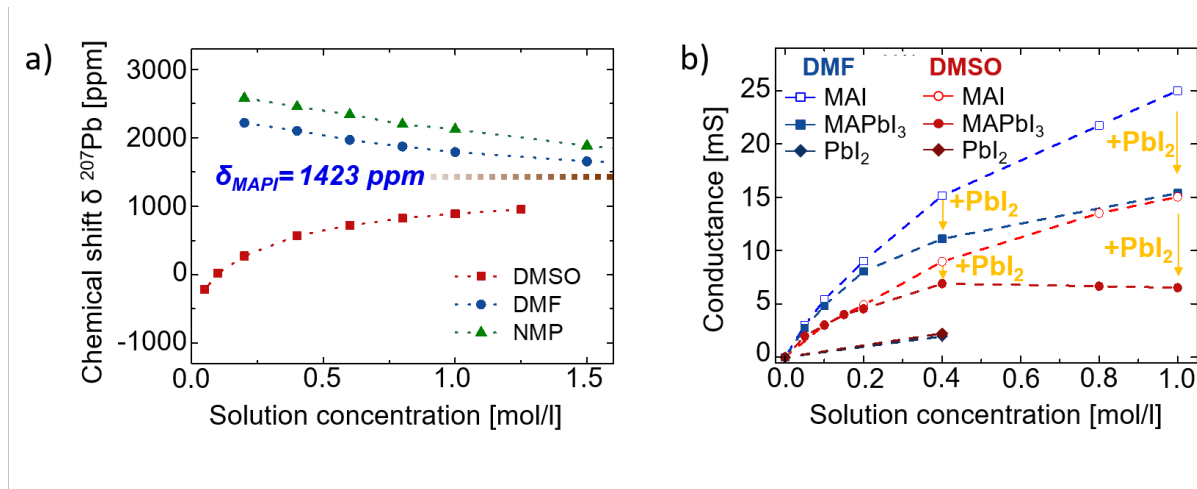
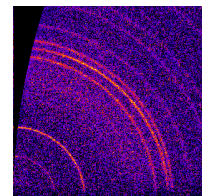
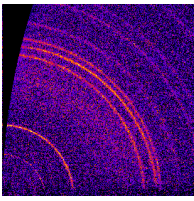


Figure 10.2: (a) ^{207}Pb nuclear magnetic resonance studies of MAPbI_3 precursors as a function of solution concentration. The dotted line represents the solid state MAPbI_3 value derived from reference [418]. Chemical shifts are reported on a ppm scale relative to the standard $\text{Pb}(\text{CH}_3)_4$. (b) Conductivity study comparing stoichiometric MAPbI_3 precursor to its singular ingredients dissolved in DMF or DMSO at different concentrations.

species,⁴²¹ only a single resonance peak of ^{207}Pb is observed in all solutions, the chemical shift of which is displayed as a function of concentration in Figure 10.2 (a). A down field chemical shift indicates a reduced electron density (de-shielding) around the lead center and up field chemical shifts indicate a higher electron density, shielding the Pb nucleus from the external field. A clear difference between the solvents DMSO and DMF/NMP can be observed already for PbI_2 solutions, reflecting a higher electron density around the lead core with DMSO, which is in line with the higher donor number of DMSO implying a larger donor strength for complexation.

Upon increasing the concentration of the perovskite solution, opposing trends in the chemical shift values are observed for DMSO and DMF/NMP. While the chemical shift in DMF and NMP solutions decreases with increasing concentration, indicating an increase in electron density around the lead core, for DMSO a decrease in electron density at the lead core is suggested with increasing concentration. Most strikingly, with increasing the concentration, the shifts for DMF/NMP and DMSO approach each other on a seemingly asymptotic path. An estimated asymptote is located around 1400 – 1450 ppm, which closely resembles values that have been reported for MAPbI_3 solid state NMR analysis of about 1423 ppm.⁴¹⁸ Since the observed chemical shift is an average over all species present in the solution, the apparent convergence of shifts towards the bulk MAPbI_3 value may indicate an increasing amount of corner sharing 3D perovskite-like species in the precur-



sor solution with increasing concentration, which are considered to form larger colloidal structures.^{276,277} These findings are in good agreement with very recent NMR studies on multi-cation bromide based perovskite inks.⁴²²

Another indication for the formation of larger lead halide structure motifs in precursor solutions is found via conductivity measurements (Figure 10.2 (b)) of MAPbI₃, MAI and PbI₂ solutions. Firstly, it is found that the conductivity of the solution increases more strongly with the MAI concentration than with PbI₂, which reflects the more ionic nature of MAI, while PbI₂ bonds show partially covalent behavior as well,⁴²³ and solvation or complexation of PbI₂ is expected rather than dissociation in solution.⁴²⁴ Differences between the solvents can be explained by their respective viscosities.^{425,426} Most intriguingly, for low concentrations (< 0.2 mol/l), the conductivity of the MAPbI₃ solutions resembles almost that of the corresponding MAI solutions, while for higher concentrations (> 0.2 mol/l), the MAPbI₃ solution conductivity is significantly lower than that of the corresponding pure MAI solution. This finding is ascribed to the formation of larger polynuclear colloidal complexes with perovskite-like structural motifs in solution as well since these extended colloidal structures provide a reduced charge/volume ratio, significantly lowering the contribution to electrical conductivity.

Thus, solvent complexing is most relevant in diluted solutions, whereas in higher concentrated perovskite precursors, as they exist during deposition in drying thin films, perovskite-like colloidal structures gain importance. Since liquid deposition techniques

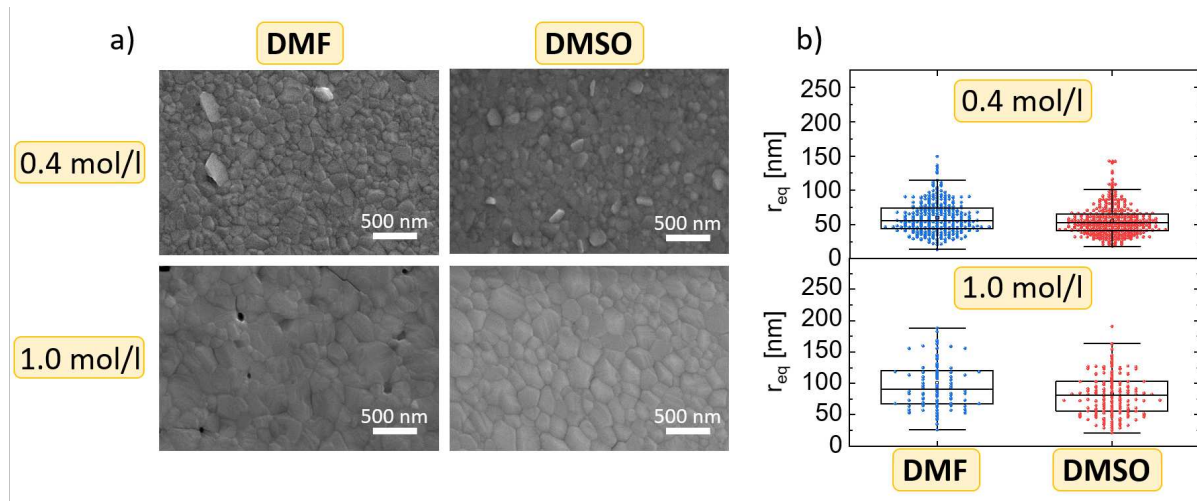
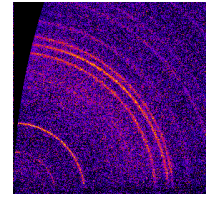


Figure 10.3: (a) Scanning electron microscopy images of MAPbI₃ layers obtained by gas quenching employing DMF or DMSO as precursor solvent at concentrations of 0.4 and 1.0 mol/l. (b) Grain size distributions derived from (a). Image modified from manuscript [i].



mostly rely on an increase of concentration until crystallization occurs, it can be expected that the progressing formation of 3D corner sharing structures will diminish the impact of lead-solvent complexes on the final crystallization process. By a direct comparison of perovskite layers deposited from DMF and DMSO solution at both 0.4 mol/l and 1.0 mol/l concentration (Figure 10.3), no significant difference in grain sizes between both solvents is observed.

Effect of Thiourea on Solution Properties A similar set of investigations was conducted on precursor solutions to which the Lewis-base thiourea was added. Thiourea has proven its impact on the perovskite crystallization before, which has been frequently attributed to an interaction with lead.^{281, 414, 427–429} Herein, the DMF/NMP solvent system was chosen as the reference system to obtain a minimum of process spread.²⁸⁰ As visible in Figure 10.4 (a)–(c), adding 0.1 mol/l thiourea to the precursor solution (without changing the original precursor concentration of 1.0 mol/l) results in a drastic increase in the grain size as well as improvements in the solar cell performance of the fabricated

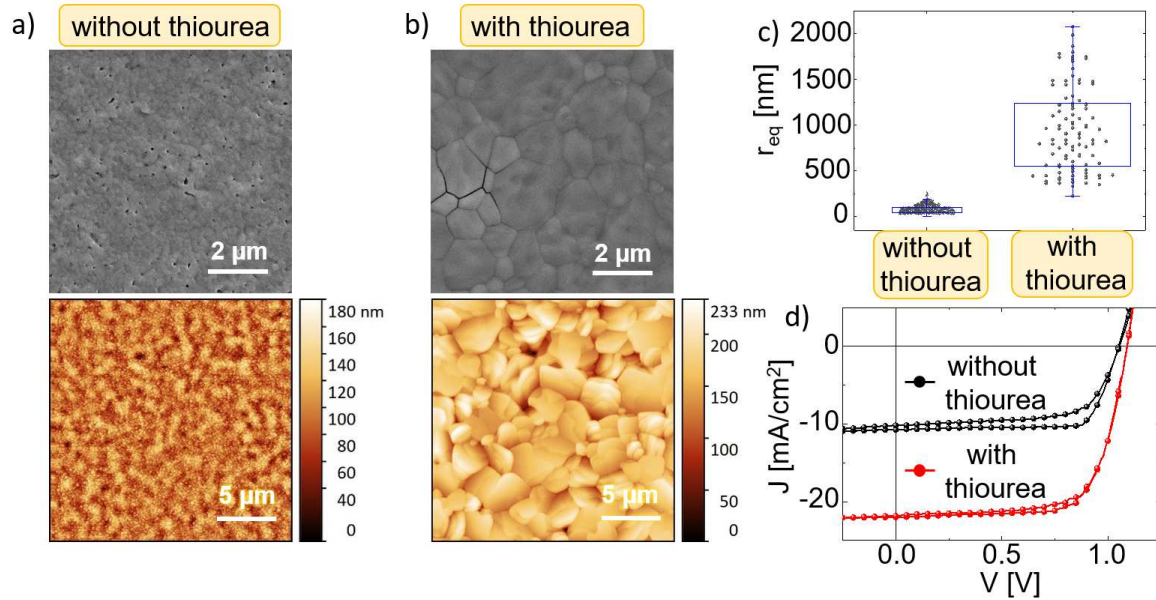


Figure 10.4: Scanning electron microscopy (SEM, top) and atomic force microscopy (AFM, bottom) topography images of MAPbI₃ layers deposited by gas quenching from solutions with concentrations of 1.0 mol/l (a) without and (b) with 0.1 mol/l of thiourea additive concentration. (c) derived grain size distribution from (a) and (b). (d) Solar cells employing an ITO/PTAA/MAPbI₃/PCBM/AZO/Ag device stack comparing MAPbI₃ layers with and without thiourea additive. Image modified from manuscript [i].

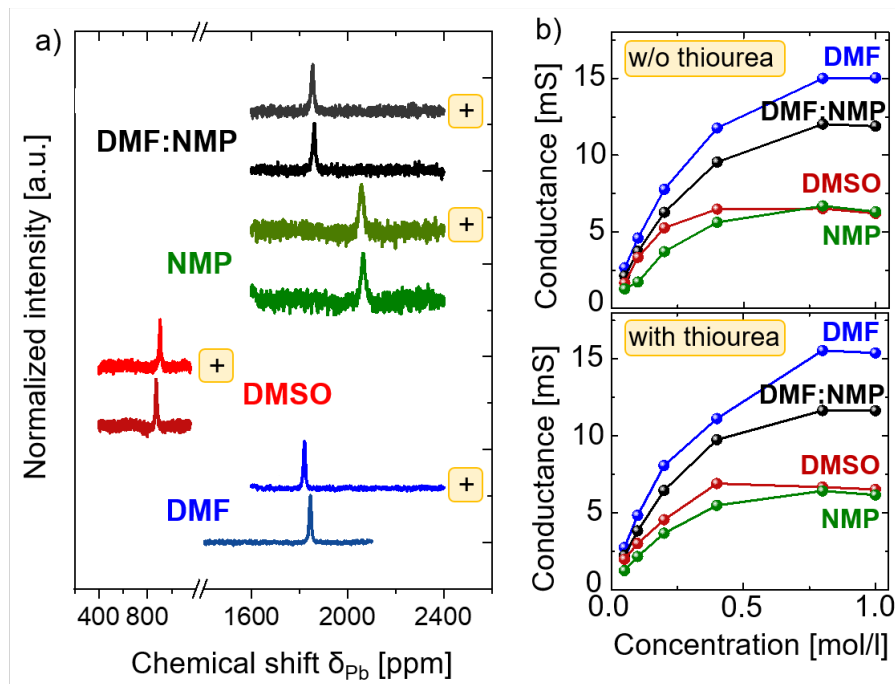
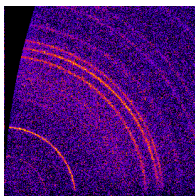


Figure 10.5: (a) ^{207}Pb NMR spectra, featuring the addition of thiourea to MAPbI_3 precursor solutions from typical perovskite solvents. Boxes with plus signs mark the spectra where thiourea has been added. (b) Conductivity studies of MAPbI_3 precursor solution in DMF, DMSO and NMP with and without thiourea. Image modified from manuscript [i].

perovskite thin films, consistent with established literature^{280–284} (Figures 10.4 (d) and D.24, appendix).

However, neither the chemical shifts determined by NMR of 1.0 mol/l perovskite solutions in DMF, DMSO or NMP (Figure 10.5 (a)) nor the conductivity measurements (Figure 10.5 (b)) show any distinct variation upon thiourea addition. Therefore, a significant impact of thiourea on the nature of lead complexes present in the precursor solution cannot be found. The complexation behavior is observed to be unaffected by the presence of the additive, contrary to literature reports which attested thiourea to possess a strong tendency to coordinate with PbI_2 , even more than O-donor ligands like DMSO.^{411, 430, 431} Notably, the amount of thiourea present in the precursor formulation was only 10 % of the amount of perovskite material, and thus even if a preferred coordination of thiourea with the precursors occurred, this would be quite limited. Nonetheless, the lead complex chemistry with solvent molecules or additives in the precursor solution shows only a negligible impact on the shape and size of the resulting crystalline grains in the thin film, which do seem substantially affected by the presence of thiourea.

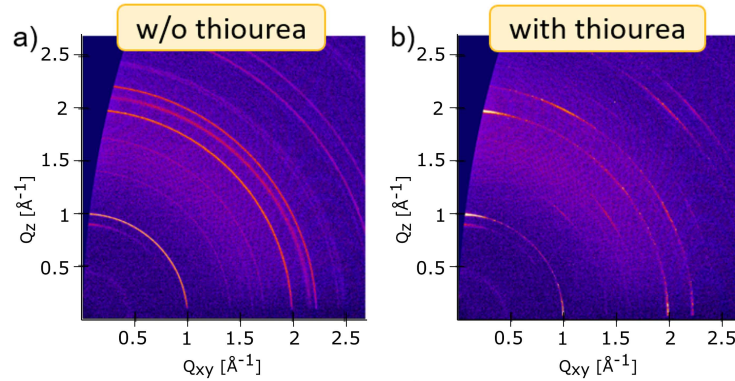
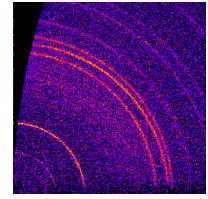


Figure 10.6: GIWAXS reciprocal space maps of MAPbI₃ thin films prepared (a) without and (b) with thiourea. Image modified from manuscript [i].

Thin Film Crystallization and Effect of Thiourea during Thermal Annealing

Since a clear impact of thiourea on the final materials can be observed, real-time investigations during the crystallization of perovskite thin films were employed to elucidate the connection between precursor chemistry and grain morphology. This was accomplished in the form of in-situ GIWAXS during perovskite thin film deposition via spin-coating including nitrogen-assisted gas quenching and thermal annealing. For this purpose, MAPbI₃ thin films were deposited from 1 mol/l solution in a DMF/NMP solvent mixture with and without thiourea addition.

A clear difference in texture can be observed between samples with and without thiourea, which is visible in the GIWAXS reciprocal space maps of the final thin film samples in Figure 10.6. For the sample without thiourea, uniform, ring-shaped features are observed (Figure 10.6 (a)), indicating a random orientation of many small crystallites. The addition of thiourea, however creates a thin film with highly oriented crystallites, indicated by the distinct intensity maxima of the diffraction features along the vertical and horizontal axes (Figure 10.6 (b)). Together with the previous results from SEM and AFM (Figure 10.4 (a) and (b)), the data implies that thiourea causes the crystallites to grow large and in a preferred orientation.

In-situ GIWAXS analysis revealed that during the spin-coating step, until annealing starts, both conditions, with and without thiourea show exactly the same crystallization behavior. The initial crystalline structure that is formed during the gas quenching is identified as a complex of the NMP solvent with PbI₂, which is indicated by its distinct main diffraction signal at around $q = 0.6 \text{ \AA}^{-1}$, marked by red crosses in Figures 10.7 (a) and (b). This PbI₂·NMP structure has been reported to occur frequently as an intermediate in

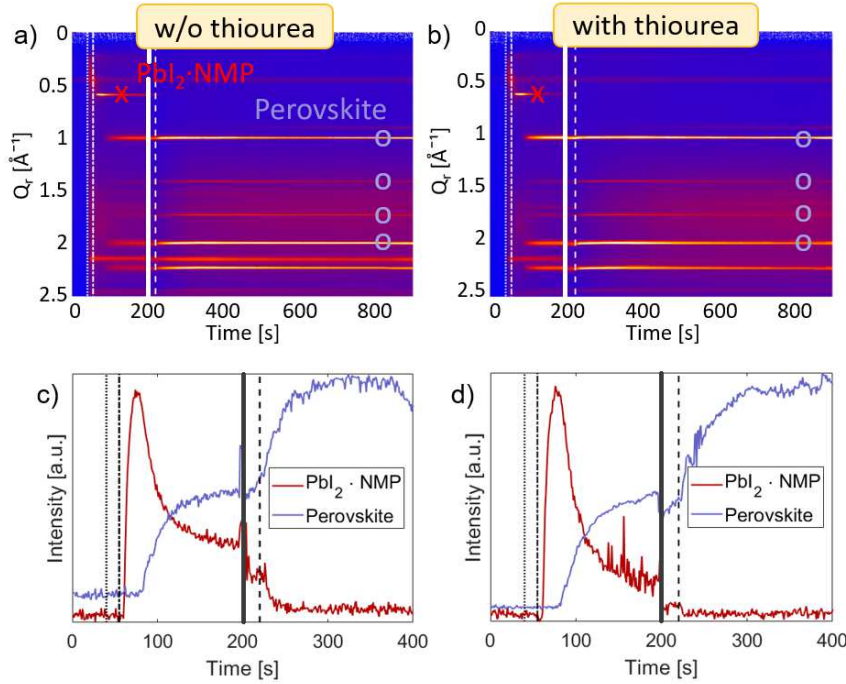
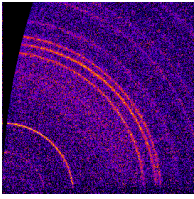


Figure 10.7: Radial intensities of GIWAXS reciprocal space maps as a function of time for MAPbI₃ thin film deposition (a) without and (b) with thiourea from a solution in DMF:NMP. Red crosses mark PbI₂·NMP, blue circles indicate perovskite structure. (c), (d) Integrated signal intensities for the PbI₂·NMP intermediate phase (red) and the perovskite phase (blue) as a function of time during MAPbI₃ thin film preparation without (c) and with (d) thiourea. Vertical lines indicate the start of spinning (dotted), start of gas quenching (dash-dotted), start of annealing (dashed) and a 3-minute pause between spin-coating and annealing (thick solid lines). Image modified from manuscript [i].

perovskite formation,^{100,105} consisting of double chains of edge-sharing lead halide octahedra with coordinated solvent molecules. Despite the presence of potentially perovskite-like colloids in the precursor solution, the PbI₂·NMP complex precipitates first. Interestingly, a partial conversion of this intermediate structure into the MAPbI₃ perovskite already occurs during the gas quenching process while spin-coating, indicated by the emergence of the signal around $q = 1 \text{ \AA}^{-1}$ (marked by blue circles in Figures 10.7 (a) and (b)). No significant difference can be observed between the precursors with and without thiourea up to this point. Both form the same PbI₂·NMP intermediate structure and convert to the MAPbI₃ perovskite structure during gas quenching on a similar time scale (see integrated intensities as a function of time in Figure 10.7 (c) and (d)). Notably, in both cases, i.e. with and without addition of thiourea, the tetragonal perovskite structure formed after spin-coating and gas quenching consists of randomly oriented crystallites, as indicated by

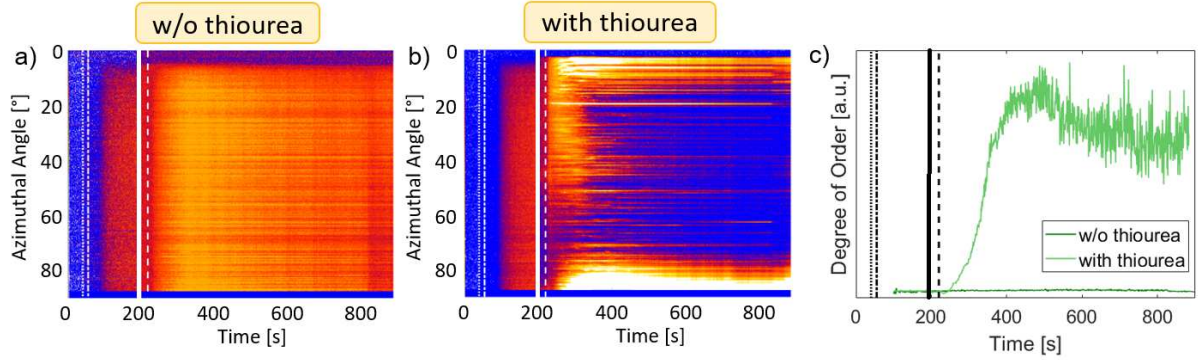
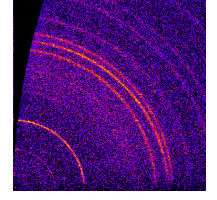
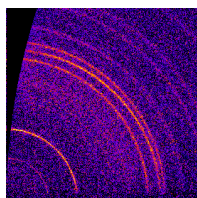


Figure 10.8: Azimuthal intensities of the (110) perovskite signal during MAPbI₃ thin film deposition as a function of time (a) without and (b) with thiourea. (c) Degree of orientation represented by the ratio of azimuthal intensities around 90° and 45° as a function of time. Vertical lines indicate the start of spinning (dotted), start of gas quenching (dash-dotted), start of annealing (dashed) and a 3-minute pause between spin-coating and annealing (thick solid lines). Image modified from manuscript [i].

a uniform distribution of azimuthal intensity, which is displayed for the perovskite (110) diffraction signal in Figures 10.8 (a) and (b), between 0 and 200 s, i.e. during the gas quenching step.

Correlated diffraction and SEM experiments at different stages of the sample fabrication indicated that while the grains visible in microscopy images are not necessarily single crystalline, the observed grain size indeed correlates with the size of coherently scattering crystallites observed by X-ray diffraction. Since the resolution of the setup, for geometrical reasons, is limited to crystallite sizes of a few hundred nanometers, the peak width is an unreliable indicator for crystallite size and film formation in the thin films containing the thiourea additive, exhibiting grain sizes of up to 1 μm . Thus, the contrast in orientation was chosen as an indicator to monitor the growth kinetics. While both compositions fully convert to the perovskite phase during thermal annealing, the azimuthal intensities in Figures 10.8 (a) and (b) show striking differences between the samples with the start of annealing after about 200 s of recording time. For the thin film without thiourea, the azimuthal intensity maintains a uniform distribution, with a certain intensity fluctuation indicating crystal growth during annealing, but still a random orientation of crystallites. On the other hand, for the thiourea-containing composition, a remarkable effect of crystallite reorientation can be observed during thermal annealing. Pronounced intensity maxima along 0 and 90° can be observed for the azimuthal intensity in Figure 10.8 (a) and (b), indicating a strongly preferred orientation of crystallites along the substrate normal. To display this observation even more clearly, the degree of orientation throughout



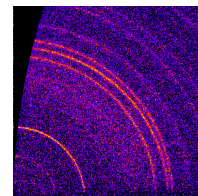
the full deposition process, represented by the ratio of the intensity at 90° against the intensity at 45° azimuthal angle (where maxima and minima of intensity occur) is plotted in Figure 10.8 (c), clearly showing a high degree of orientational order for the material with thiourea developing during the thermal treatment, but not without the additive. Thus, the annealing step was found to be crucial for the development of the perovskite layers and the specific differences resulting from the precursor inks without and with the thiourea additive.

Thiourea in the Final Thin Films To obtain the final location of the thiourea additive, Fourier transform infrared spectroscopy (FTIR) was performed (Figure D.25, appendix), where the presence of the thiourea molecule is indicated inside the annealed perovskite film along with a distinct shift of the C-S stretching vibration compared to the bare material. This points towards a coordination between the perovskite material and thiourea in the solid film, likely happening at the grain boundaries. This assumption is further supported by a similar shift that is observed when thiourea is added to a PbI_2 solution for thin film deposition, indicating a possible interaction with lead, while no such shift can be found for MAI layers with thiourea additive.

Conclusions It has been shown that the predominant impact of the thiourea additive appears only during the post deposition annealing process, where it drastically affects the perovskite crystal growth and orientation. A possible scenario is that the coordination of thiourea which is relevant to the increased structural order and crystallite size takes place during the annealing step, likely on the surface of growing perovskite grains, thereby impacting the rearrangement of the probably still mobile perovskite species.

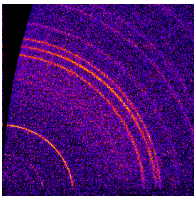
The comprehensive study including precursor chemistry, film properties and investigation of the fabrication procedure in real time with and without additives provides a strategy to investigate the mechanisms of lead complexing and the perovskite crystal formation. Especially when interpreting the impact of additives, common conceptions of the relationship between the complex formation in solution and the crystallization of the perovskite thin film might need to be revisited. The combination of solution-based techniques such as NMR and conductivity measurements, common thin film investigations including SEM and solar cell performance, and in-situ GIWAXS was crucial to achieve a more sophisticated picture of the processes before and during perovskite deposition.

The formation of lead complexes in precursor solutions of DMF, DMSO and NMP could be tracked, where the addition of the Lewis base additive thiourea did not show any significant effect. Therefore, no clear evidence for a relevant impact of the complex for-



CHAPTER 10. THIOUREA ADDITIVE

mation in the perovskite precursor on the final film formation could be found. Indeed, the influence of the solvent coordination on the lead centers loses relevance with increasing precursor concentrations, as is ultimately the situation in the supersaturated deposited thin film. In-situ GIWAXS studies revealed that even in this supersaturated layer, before thermal annealing, no distinction between as-cast films from precursors with or without the thiourea additive is possible. As a result, the most critical processing step, upon which the impact of the Lewis base additive thiourea manifests, was identified to be the post-deposition annealing.



10.2 Influence of Crystallization Kinetics on the Effects of Thiourea

As has been shown in the previous section, large crystallite and grain growth and orientation can be induced by solvent additives such as thiourea.^{280–284} Both of these characteristics are commonly presumed to be achievable only with slow, controlled growth of perovskite thin films,^{278,432–434} either with sophisticated solution-based methods such as sequential deposition protocols,^{435,436} or post-deposition treatments including hot-pressing⁴³⁷ or vapor annealing.^{435,438–440} Additives modifying the grain size are often suspected to manipulate and slow down the crystallization kinetics.²⁸²

In this section it is shown, for the archetypal perovskite composition MAPbI_3 , that thiourea addition to the precursor solution leads to oriented large crystallites irrespective of crystallization speed. Thin films are fabricated via gas quenching assisted and antisolvent assisted solution deposition protocols, which exhibit vastly different precursor conversion and crystallization kinetics, but show similar effects of thiourea addition on the grain size. This section is based on manuscript [ii].

Thin Film Phenomenology MAPbI_3 thin films were deposited on ITO-coated glass substrates employing three different deposition protocols: nitrogen-gas quenching²⁸⁰ and the widespread antisolvent-based deposition³⁷⁶ with either chlorobenzene or isopropanol to

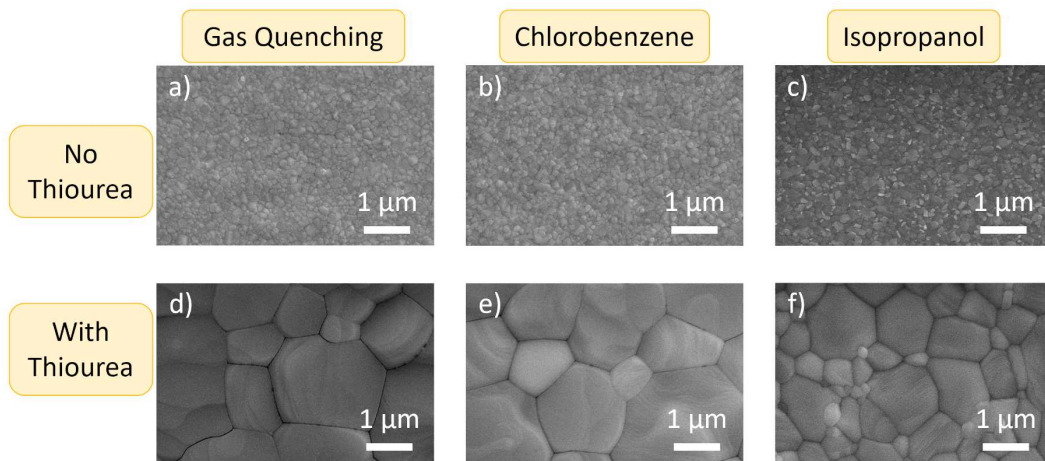
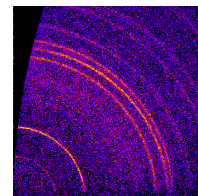


Figure 10.9: SEM images of MAPbI_3 thin films deposited employing different quenching methods: (a) and (d) gas quenching; (b) and (e) chlorobenzene antisolvent; (c) and (f) isopropanol antisolvent. (a)–(c) without additive; (d)–(f) with addition of 0.1 mol/l thiourea. Image modified from manuscript [ii].



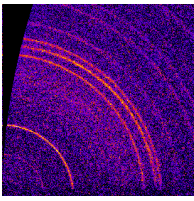
CHAPTER 10. THIOUREA ADDITIVE

be deposited as the antisolvent during spin-coating the precursor solution of MAI and PbI_2 in a mixture of DMF and NMP. Experimental details can be found in the experimental Section C.3 in the appendix.

The SEM images in Figure 10.9 display relatively small crystallites of an average equivalent radius of about a few tens of nanometers when the thin films are deposited without thiourea addition irrespective of the quenching method. Similarly, when thiourea is added to the precursor solution, all three quenching methods produce thin films with distinctly enhanced grain sizes up to equivalent radii of micrometer size, which is displayed in the lower panel of Figure 10.9. Thus, the final grain size in the MAPbI_3 thin films is not significantly influenced by the quenching method, and is determined mainly by the presence or absence of thiourea.

Crystallization Kinetics Since it is commonly assumed that grain size and orientational order can be tuned by the crystallization speed, the influence of the different quenching methods and the addition of thiourea on the crystallization kinetics were investigated by real-time GIWAXS during thin film deposition, including the spin-coating and annealing steps. Remarkably, the results in Figure 10.10 indicate that the crystallization kinetics rather depend on the quenching method and are unaffected by the presence of thiourea. Figure 10.10 (a)–(c) displays integrated peak intensities of the distinct crystal phases which occur during spin-coating. Initially, for all samples a crystalline solvent-complexing intermediate structure of $\text{PbI}_2 \cdot \text{NMP}$ is formed upon start of the quenching by either gas flow or antisolvent dropping. This structure is then converted into a crystalline perovskite, which happens slowly over about 30–40 s for the gas quenching method, but rather rapidly within about 2–3 s for both antisolvents. While for gas quenching and chlorobenzene antisolvent, the conversion into perovskite is observed to be nearly complete already at the end of spin-coating, the thin films deposited using isopropanol as the antisolvent form a second intermediate structure, which is likely a $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{NMP}$ type of structure. Since this type of structure has been observed using other primary solvents before, predominantly in Pb-rich precursor solutions,¹¹² its presence could be linked to isopropanol being an improper antisolvent, which can dissolve and wash away portions of the organic cations, in this case methylammonium. Furthermore, selective removal of DMF from the parent solvent by isopropanol application enables formation of the NMP-based intermediate structure. Thus, all three methods exhibit clear differences between each other in the crystallization kinetics, which are not reflected in the crystalline grain size of the final thin films in Figure 10.9 (a)–(c).

Comparing these results from the pure MAPbI_3 thin films to those with thiourea addition



10.2. CRYSTALLIZATION KINETICS

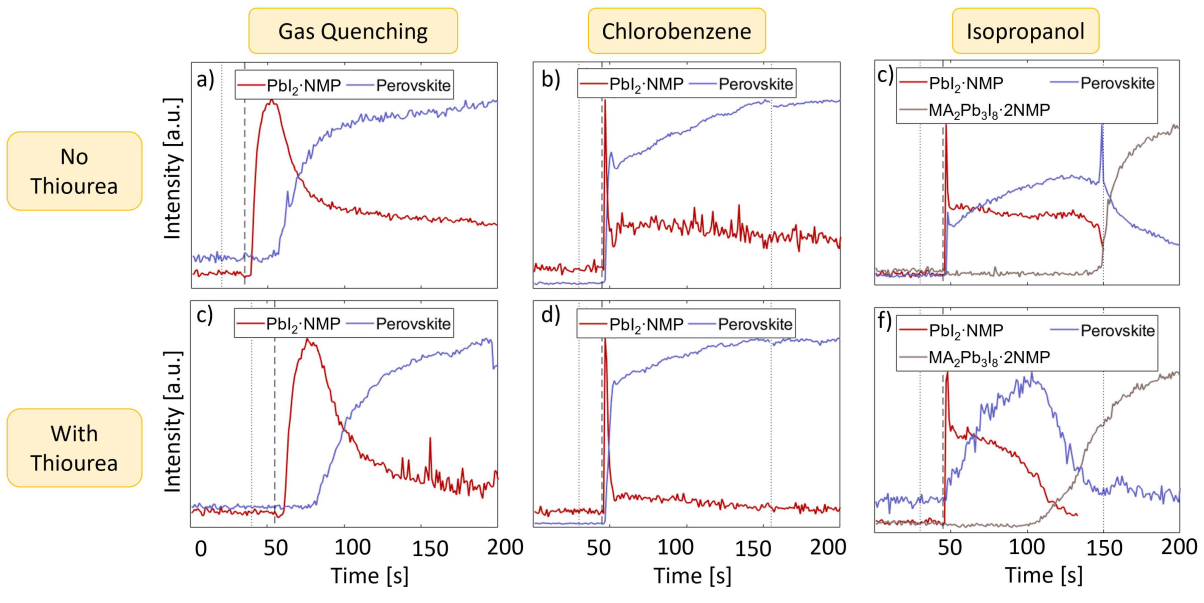


Figure 10.10: Integrated X-ray diffraction signal intensities from distinct crystal phases as a function of time during spin-coating of MAPbI_3 employing different quenching methods: (a) and (d) gas quenching; (b) and (e) chlorobenzene antisolvent; (c) and (f) isopropanol antisolvent. (a)–(c) without additive; (d)–(f) with thiourea additive. The corresponding radial profiles as a function of time can be found in the appendix in Figure D.26 for the spin-coating and Figure D.27 for the annealing, while a list of the integrated signals representing each phase can be found in Table D.2. Vertical dotted lines indicate start and end of spin-coating; dashed lines mark the start of the quenching process. Image modified from manuscript [ii].

in Figures 10.10 (d)–(f), generally only a minor influence of the presence of thiourea on the crystallization kinetics during spin-coating is found. The same crystalline intermediates are formed and converted via the same sequences as in the films without thiourea, again only depending on the quenching method. Thus, the presence of thiourea only exerts a negligible influence on the crystallization sequences and kinetics during the spin-coating step. The difference between the quenching methods is much more apparent than any influence of the additive.

This implies that the crystallization route and speed are not correlated with the grain size, which is only determined by the presence of thiourea.

Influence of Thiourea During Thermal Annealing As is shown in the previous section, the effect of thiourea on the crystal growth and orientation of perovskite thin films is observed only during thermal annealing. Immediately with the start of thermal treatment, the small amount of remaining solvent complex is converted into the perovskite structure

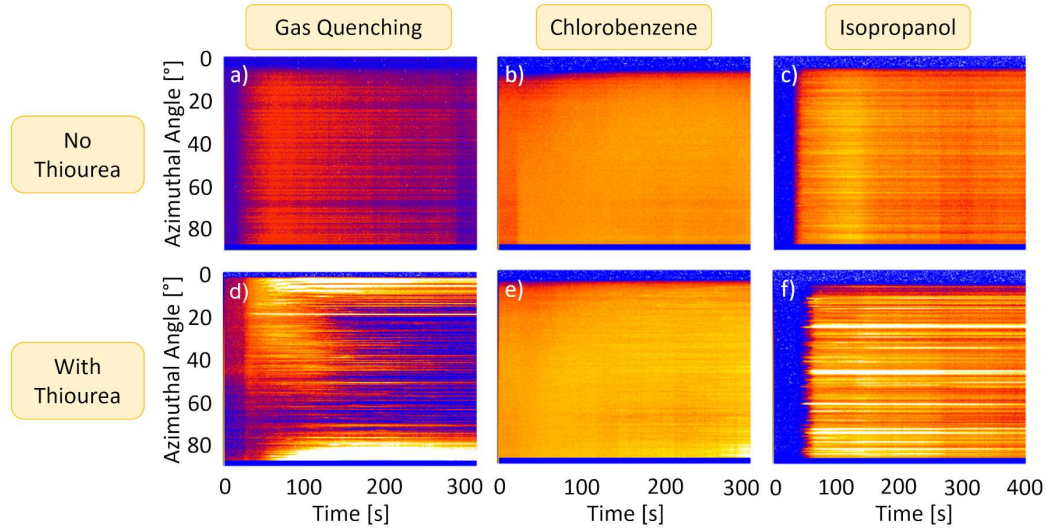
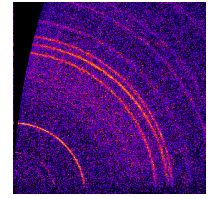
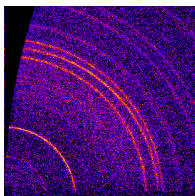


Figure 10.11: Azimuthal intensities of the (110) perovskite diffraction signal as a function of time during annealing of MAPbI_3 employing different quenching methods: (a) and (d) gas quenching; (b) and (e) chlorobenzene antisolvent; (c) and (f) isopropanol antisolvent. (a) – (c) without additive; (d) – (f) with thiourea additive. The respective azimuthal intensity data during the spin-coating is shown in Figure D.29 in the appendix, showing uniform azimuthal intensity distribution for all samples at this stage. Image modified from manuscript [ii].

for all conditions (Figures D.27 and D.28, appendix), to create a phase-pure perovskite thin film. The azimuthal intensity of the (110) perovskite diffraction ring measured by real-time GIWAXS, which is shown already in Section 10.1 for MAPbI_3 thin films deposited via the gas quenching route and is displayed again in Figure 10.11 (a) and (d) serves as a visual representation of the structural evolution induced by thermal heating in presence of thiourea. A nearly uniform azimuthal intensity during spin-coating (Figure D.29, appendix) as well as in the beginning of annealing for both conditions, which remains consistent for the pure- MAPbI_3 sample, indicates small, randomly oriented crystallites. The sample with thiourea in Figure 10.11 (d) quickly develops sharp intensity maxima at the in-plane and out-of plane directions, i.e. 0 and 90°. This corresponds to a spot-like diffraction pattern (Figures 10.12 (c) and D.30, appendix), which is characteristic for a well oriented structure.

Both pure- MAPbI_3 samples fabricated by antisolvent quenching (Figures 10.11 (b) and (c)) show a similarly uniform angular intensity distribution throughout the whole thermal annealing process, indicating similarly small crystallites, which is consistent with the results from the SEM data in Figure 10.9. In the presence of thiourea, both show distinct



10.2. CRYSTALLIZATION KINETICS

alterations in azimuthal intensity, indicative of morphological changes in the grains of the thin film.

When employing chlorobenzene antisolvent, while the final thin films show similar grain morphologies and crystal properties to the ones fabricated by gas quenching, as indicated by similar diffraction patterns, displayed in Figure 10.12 (d), the azimuthal intensities during annealing (Figure 10.11 (d) and (e)) show different kinetics. Contrary to the gas quenching based thin film, which shows a rapid reorientation and crystal growth, for the chlorobenzene antisolvent fabrication, this process is much slower and only starts towards the end of the real-time GIWAXS measurement time, which was set to 300 s (i. e. 5 min) of annealing. The samples whose reciprocal space maps are shown in Figure 10.12 were annealed for twice the time (10 min) and thus show indeed a similar degree of orientational order as the gas quenching fabricated ones, indicating that the process shown in Figure 10.11 (e) is not yet finished, but shows only the beginning of thiourea exerting its influence. This, again, indicates that even during the annealing step, the speed of the process is of minor importance, but the final grain morphology is mainly determined by the mere presence of the thiourea additive.

The azimuthal diffraction intensities of the perovskite phase in thin films deposited using isopropanol as the antisolvent differ considerably from those using gas quenching and chlorobenzene antisolvent and are displayed in Figure 10.11 (c) and (f). A distinct effect of crystal growth is observed for the sample containing thiourea by a coarsening of the azimuthal intensity, indicating larger coherently scattering domains as opposed to the much smoother, more uniform intensity distribution without the additive. However, a clear orientational preference is absent. This is likely related to isopropanol dissolving parts of the precursor including thiourea, which has been reported to be soluble in polar solvents.⁴⁴¹ Thus, the amount of thiourea present in the sample fabricated via the isopropanol-based antisolvent route can be expected to be reduced compared to the non-polar antisolvent chlorobenzene and the gas quenching method and may not suffice to induce a similarly high degree of orientational order as for those conditions, while the stoichiometry of the perovskite itself is potentially altered as well by partial dissolution in the isopropanol antisolvent.

As a semi-quantitative measure of the effects of thiourea during sample annealing, the root-mean-squared variation of the previously displayed (Figure 10.11) azimuthal (110) perovskite diffraction intensity was chosen. Each single diffraction spot along one diffraction ring corresponds to one coherently scattering domain, thus consequently less, but more intense of these diffraction spots indicate less, but larger crystallites in the investigated sample volume. Thereby, the intensity fluctuations along the azimuthal direction

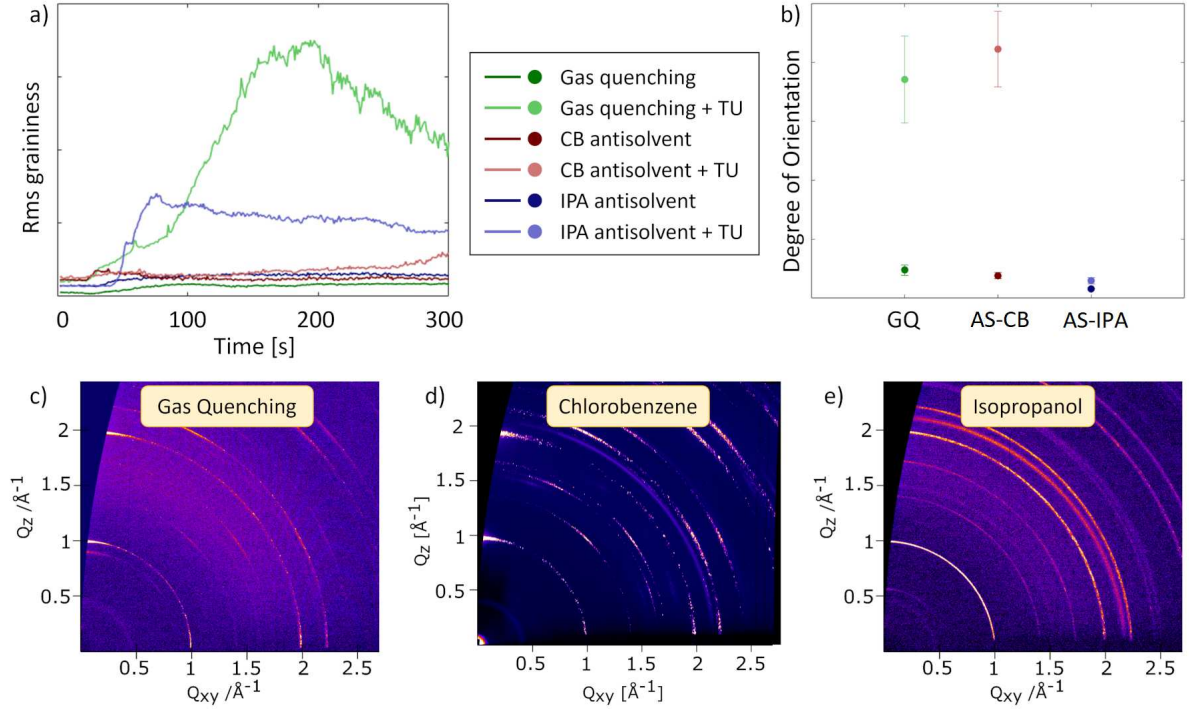
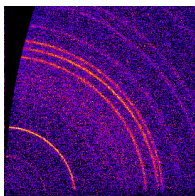


Figure 10.12: (a) Root-mean-square roughness of the azimuthal intensity of the (110) perovskite diffraction signal (displayed in Figure 10.11) as a function of time during thermal annealing of MAPbI_3 thin films to serve as a measure for the effect of thiourea on crystallite size and orientation during the early stages of annealing. (b) Degree of orientation in the final thin film after prolonged annealing determined from the intensity distribution in the azimuthal intensity of the perovskite (110) signal. (c)–(e) GIWAXS reciprocal space maps of MAPbI_3 thin films with thiourea additive fabricated using (c) gas quenching, (d) chlorobenzene antisolvent and (e) isopropanol antisolvent. Corresponding GIWAXS reciprocal space maps without addition of thiourea can be found in Figure D.30 Image modified from manuscript [ij].

directly relate to the distribution of larger crystallites and thus can be employed to monitor the effects in real-time, as displayed in Figure 10.12 (a). It has to be noted that the crystallite sizes, which can be seen in the SEM data in Figure 10.9 are not necessarily the same as the coherently scattering domains observed by GIWAXS. Since in this study a clear correlation is observed between both techniques, although no absolute coincidence can be provided, a correlation of the trends in crystallite size is used as an approximate semi-quantitative measure.

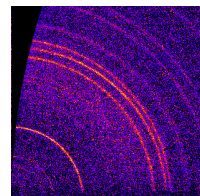
For the MAPbI_3 thin films deposited without the addition of thiourea, the variance of the azimuthal profile of the diffraction signal stays practically the same, indicating only a limited amount of crystallite growth and preferred orientation. As described above qual-



itatively, a quick increase of the intensity variation could be observed for the thiourea-containing composition when employing the gas quenching technique, reflecting on the large grain size and strongly preferred orientation. For the thin film employing isopropanol as the antisolvent, a quick increase of the intensity variation is observed as well, reflecting the crystallite growth, however to a much lower extent than the gas quenching based samples, which is likely due to the missing orientational order. The thin films using chlorobenzene as an antisolvent do not show an initial strong increase of the pattern roughness and grain size right away. A beginning rise of the curve can only be observed towards the end of the 5 minutes of measurement, indicating much slower crystal growth. Thus, samples were prepared applying longer annealing times, and a similar intensity variation parameter as in Figure 10.12 (a) was employed to determine the degree of orientational order in the final samples, which is displayed in Figure 10.12 (b). Here it can be seen that the effects of thiourea are of a similar extent in the thin films prepared by gas quenching and chlorobenzene antisolvent, such that in both cases the thin films with thiourea display a much higher degree of orientational order along with the larger crystallite size. A much lower degree of orientational order is observed for the isopropanol-quenched samples, consistent with the real-time development in Figure 10.12 (a) and most likely related, as previously mentioned, to the solubility of thiourea in isopropanol causing it to be washed out in considerable amounts during antisolvent application.

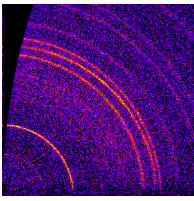
Conclusions This study showed that the effect of the thiourea additive on the size and orientation of crystalline grains of MAPbI₃ thin films does not depend on the crystallization speed. Contrary to the popular notion that only a slow crystallization can achieve large, well-oriented crystallites in a perovskite thin film, it was found that the presence of thiourea is sufficient to induce crystalline grain growth and orientational order. This effect is unaffected by the conversion kinetics during solution deposition, which are determined by the quenching method. Thiourea exerts its influence not until the thermal annealing step, as discussed in the previous section. Thus, its presence until then is required to achieve well-oriented large crystallites. Applying an antisolvent which dissolves thiourea, such as isopropanol, reduces its effect drastically and the crystallite orientation is much less pronounced. Thus, the crystallization kinetics and sequences during spin-coating as well as the speed of the crystal evolution during thermal annealing are less relevant for the grain-enhancing effects of thiourea, which only depend on its presence during the annealing step.

Together with the results from the previous chapter, where thermal annealing was identified as the crucial step for thiourea to exert its effect on crystallite size and orientation,



CHAPTER 10. THIOUREA ADDITIVE

while no effect on the complexation behavior of lead in the solution and during solution deposition is observed, this study will help to elucidate the mechanisms of additive inclusion during perovskite thin film deposition.



10.3 Compositional Dependence of the Effect of Thiourea

In the previous two sections it is shown when and how the addition of thiourea to the perovskite precursor solution for thin film deposition affects the crystallization leading to orientational order and growth of large MAPbI₃ crystallites during thermal annealing irrespective of the quenching method and conversion time. All of these investigations were conducted on the same composition, MAPbI₃ as the archetypal hybrid perovskite material.

This section extends these investigations to further compositions, where either the central methylammonium cation is replaced by a mixture of formamidinium and cesium or the halide is bromide instead of iodide. Additionally, the influence of thiourea addition on iodide/bromide halide mixtures is investigated. Thus, the effects of thiourea are studied depending on the material composition to further elucidate the working mechanism of the additive.

Samples were prepared by the same procedure as in Section 10.1 by the gas quenching method. The experimental details can be found in Section C.3 in the appendix.

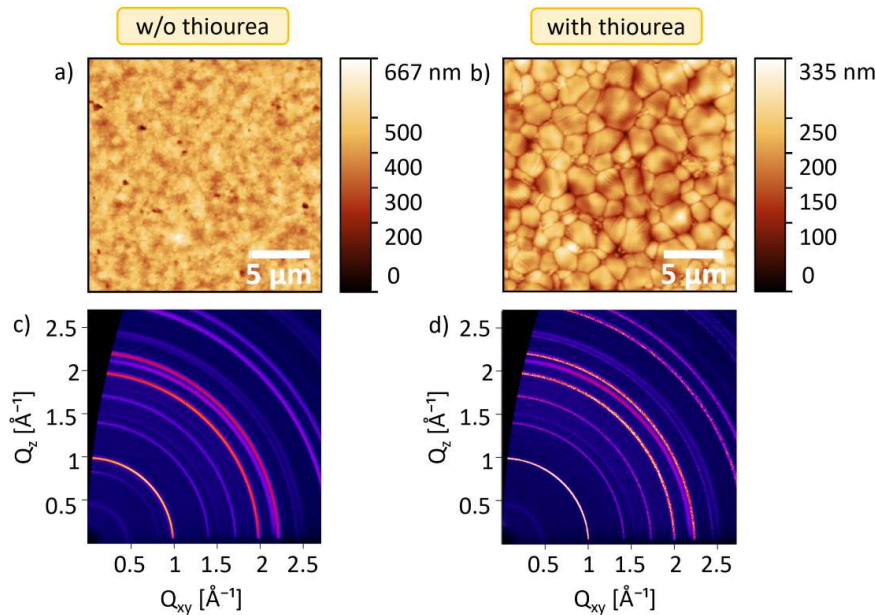
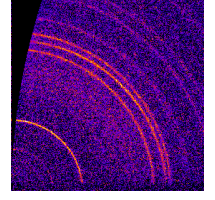


Figure 10.13: AFM images of FA_{0.94}Cs_{0.06}PbI₃ thin films (a) without additive and (b) with thiourea additive. GIWAXS reciprocal space maps of FA_{0.94}Cs_{0.06}PbI₃ thin films (c) without additive and (d) with addition of 0.1 mol/l thiourea.



Replacing the Central Cation As is mentioned on several occasions in previous chapters, replacing the methylammonium cation by formamidinium or a mixture of formamidinium and cesium is a common strategy to improve stability and performance of perovskite-based photovoltaic devices.^{37, 140, 141, 143, 168, 169} Thus, extending the investigations of thiourea additive interactions to the composition of $\text{FA}_{0.94}\text{Cs}_{0.06}\text{PbI}_3$ has practical relevance.

In the AFM images of $\text{FA}_{0.94}\text{Cs}_{0.06}\text{PbI}_3$ without and with thiourea (Figure 10.13 (a) and (b)), a similar effect of thiourea on the grain morphology as for the MAPbI_3 composition can be observed. While the grains in the pure material are rather small, the addition of thiourea leads to large micrometer sized crystallites. This is visible in the corresponding

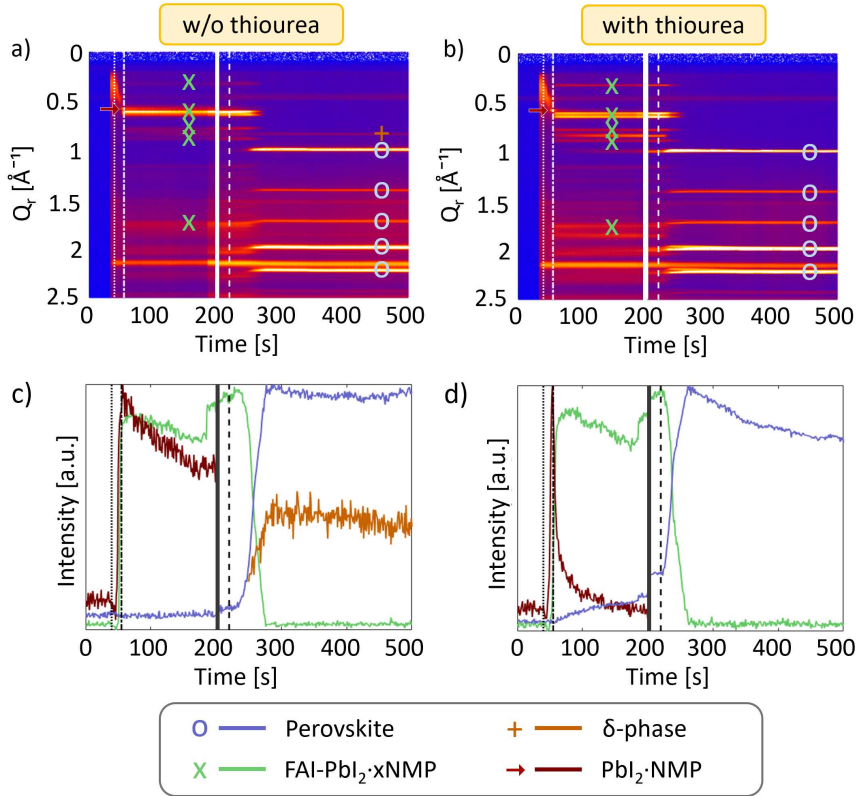


Figure 10.14: In-situ GIWAXS analysis during thin film deposition of $\text{FA}_{0.94}\text{Cs}_{0.06}\text{PbI}_3$ without (a), (c) and with (b), (d) addition of thiourea. (a), (b) Radial intensities of reciprocal space maps as a function of time; (c), (d) Integrated intensities of different crystal phases as a function of time, corresponding signature peaks for each composition can be found in Table D.3. Vertical lines indicate start of spin-coating (dotted), start of gas quenching (dash-dotted), start of heating (dashed) and a 3-minute break between spin-coating and annealing (thick lines).

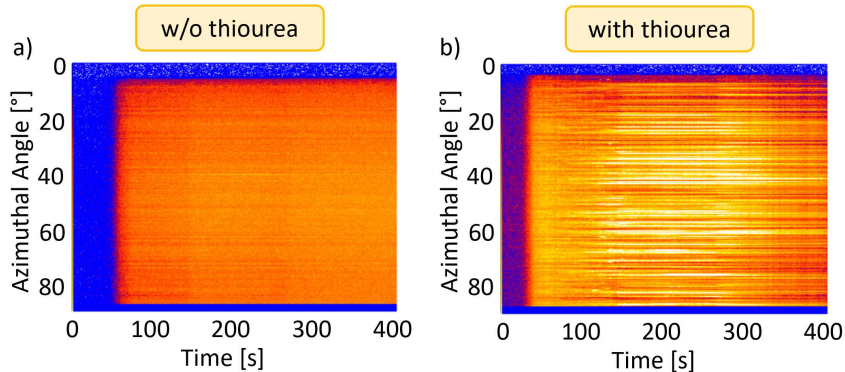
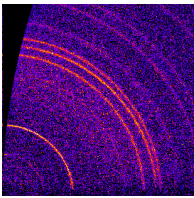
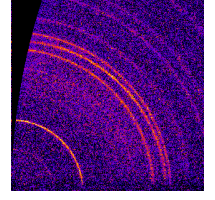


Figure 10.15: Azimuthal intensity profiles of reciprocal space maps as a function of time during thermal annealing of $\text{FA}_{0.94}\text{Cs}_{0.06}\text{PbI}_3$ without (a) and with (b) addition of thiourea.

reciprocal space maps in Figures 10.13 (c) and (d) as well, where the smooth diffraction rings exhibit increased graininess upon thiourea addition. A clear preferential crystallite orientation is, however, not observed.

GIWAXS was recorded during spin-coating of the compositions (Figure 10.14) and revealed a distinct crystallization sequence different from the MAPbI_3 composition, but consistent with and without thiourea. After the start of spinning, initially a short-lived $\text{PbI}_2\cdot\text{NMP}$ phase^{100,105} is formed (marked by a red arrow in Figures 10.14 (a) and (b)), which quickly converts into a different longer lived intermediate phase persisting until the end of annealing, which is marked by green crosses in Figures 10.14 (a) and (b). This phase has not been reported in literature and is considered to be a $\text{FAI-PbI}_2\text{-NMP}$ -based type of solvent complex.¹¹⁸ A similar crystallization sequence is observed irrespective of the presence of thiourea.

Upon the start of thermal annealing, this intermediate is quickly converted into a perovskite structure, marked by blue circles in Figures 10.14 (a) and (b). The kinetics of the conversion are observed to be similar with and without thiourea. Similar to the MAPbI_3 -based samples, the effect of thiourea is observable during the thermal annealing. The azimuthal intensities in Figure 10.15 show a significant increase of the intensity fluctuations along the perovskite (100) diffraction signal, which indicates crystal growth into larger crystallites, as was similarly observed for the MAPbI_3 thin films in the previous two sections. Orientational order of the crystallites is not observed, consistent with the results from the reciprocal space maps of the final thin films (Figures 10.13 (c) and (d)). Notably, the presence of thiourea is observed to eliminate formation of the FAPbI_3 δ -phase, which is detected only if thiourea is not present (orange plus sign in Figure 10.14 (a)). This



indicates additional stabilization of the FACsPbI_3 perovskite phase against transition to the non-perovskite photoinactive δ -phase.

Thus, compared to MAPbI_3 , thiourea causes a similar grain and crystallite enlargement for the composition based on formamidinium, but does not lead to a similar orientational order. As an additional effect, however, the presence of thiourea reduces the formation of hexagonal FAPbI_3 δ -phase.

Effect of Thiourea on Bromide-Based Compositions Besides exchanging and mixing of the central cation, the halide is a tuning parameter in perovskite compositions as well, as discussed in Section 9.4. Thus, in this paragraph, the effect of thiourea on bromide-based materials is presented, while the following paragraph discusses the consequences for iodide-bromide mixed halide compositions.

As can be seen from the SEM images in Figures 10.16 (c) and (d), MAPbBr_3 perovskite thin films already grow into very large crystallites of micrometer size without any additive. Adding thiourea does not significantly affect the size of the crystalline grains. GIWAXS reciprocal space maps show a diffraction pattern with clear angular maxima, indicative of orientational order for both the MAPbBr_3 thin film with and without the addition

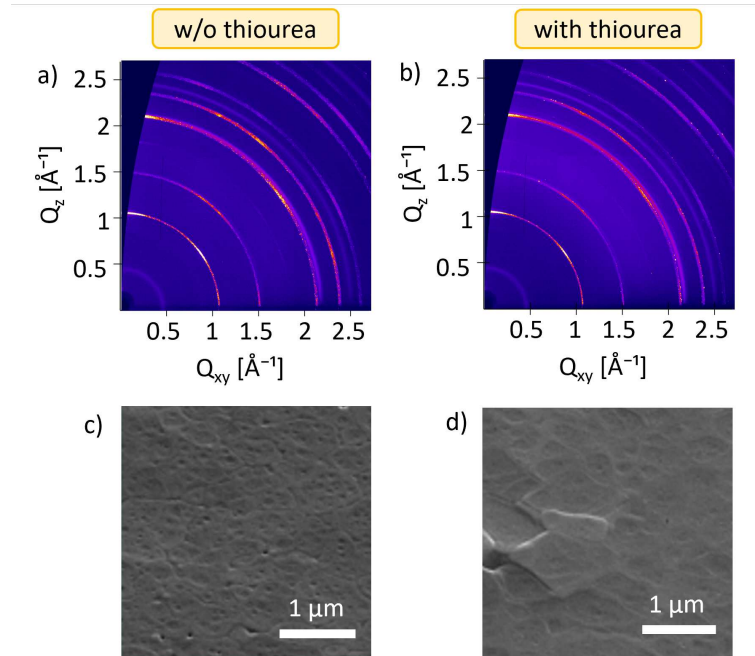


Figure 10.16: GIWAXS reciprocal space maps of MAPbBr_3 thin films deposited without (a) and with (b) addition of thiourea, $\alpha_i=0.3^\circ$. Scanning electron microscopy images of MAPbBr_3 thin films without (c) and with (d) addition of thiourea.

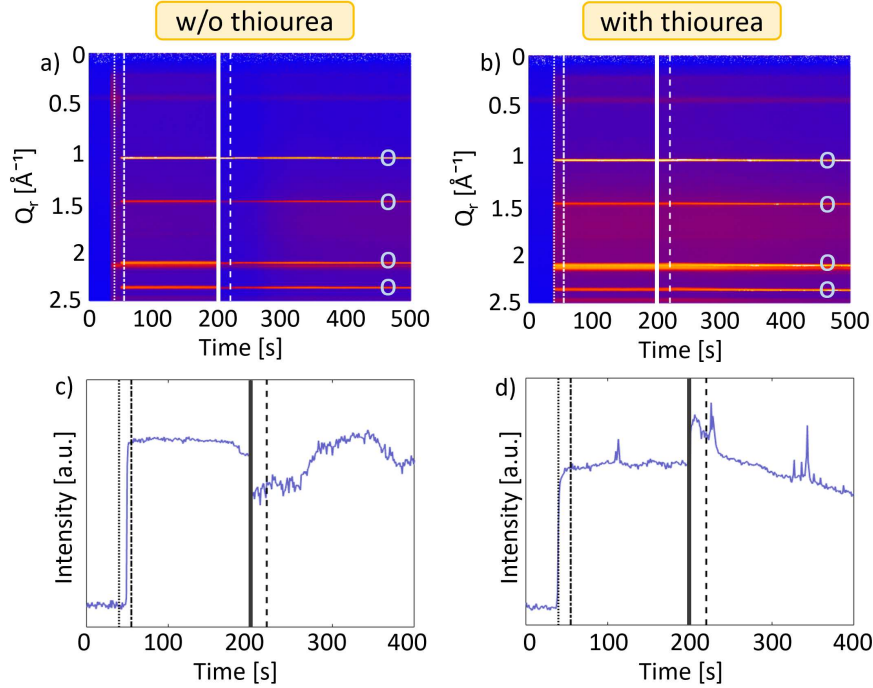
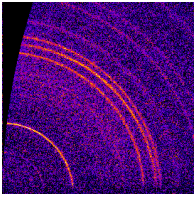


Figure 10.17: In-situ GIWAXS during thin film deposition of MAPbBr₃ (a), (c) without and (b), (d) with addition of thiourea. (a), (b) Radial intensities of reciprocal space maps as a function of time; (c), (d) Integrated intensities of the perovskite phase as a function of time. Vertical lines indicate start of spin-coating (dotted), start of gas quenching (dash-dotted), start of heating (dashed) and a 3-minute break between spin-coating and annealing (thick lines).

of thiourea (Figure 10.16 (a) and (b)). These large, oriented MAPbBr₃ crystallites are observed to crystallize and grow to their large size already during spin-coating and are not significantly altered by thermal annealing as can be observed in the time dependent diffraction patterns in Figures 10.17 (a), (b) and the corresponding integrated intensities in Figure 10.17 (c) and (d). These show a direct crystallization of the perovskite phase during the spin-coating step with negligible alteration upon thermal treatment. The azimuthal intensity distributions in Figure 10.18 show a strong orientational order from the beginning of crystallization and the large intensity fluctuations along the azimuthal angle indicate large crystallites, which do not show considerable changes during annealing.

This behavior is unaffected by the presence of thiourea, which exerts no observable influence on the crystallization and growth of MAPbBr₃. However, this is complicated by the fact that the most readily observed effects of thiourea on the MAPbI₃ thin films, i.e. growth of large crystals and orientational order, are intrinsically exhibited by the bromide-based composition and thus application of thiourea might be obsolete.

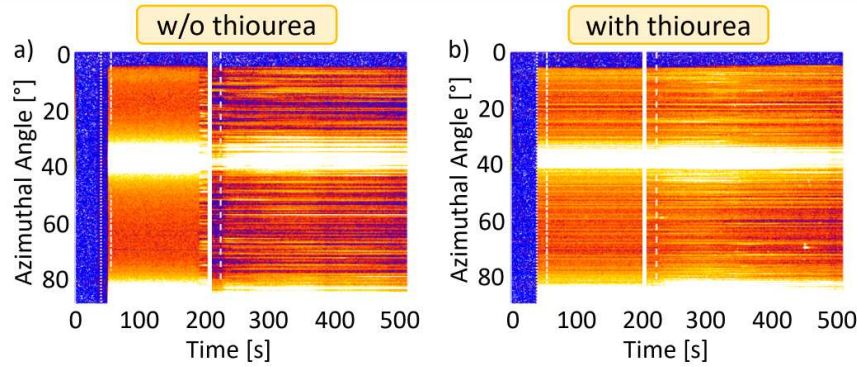
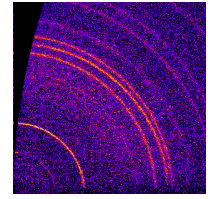
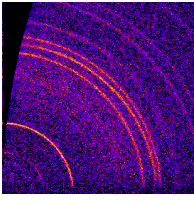


Figure 10.18: Azimuthal intensity profiles of reciprocal space maps during thin film deposition of MAPbBr_3 as a function of time without (a) and with (b) addition of thiourea. Vertical lines indicate start of spin-coating (dotted), start of gas quenching (dash-dotted), start of heating (dashed) and a 3-minute break between spin-coating and annealing (thick solid lines).

Influence of Thiourea on Mixed Halide Compositions The crystallization and growth of methylammonium-based mixed halide perovskite thin films is extensively discussed in Section 9.4. Therein, it is presented that crystallization of mixed halide perovskite materials occurs via halide segregated crystallization sequences and intermixing of the iodide and bromide fractions to form a mixed halide perovskite is only achieved during thermal annealing. A similar behavior is observed for the materials with a 1:1 iodide:bromide mixture deposited from DMF/NMP using gas quenching. During spin-coating of the composition without any additive (Figure 10.19 (a) and (c)), initial growth of a bromide-based well-oriented perovskite phase is observed simultaneously with the formation of the $\text{PbI}_2 \cdot \text{NMP}$ solvent complex structure, which was observed for pure MAPbI_3 compositions as well. Thus, again, the halide segregated growth behavior is reproduced. Addition of thiourea does not significantly affect this behavior during spin-coating and the same kinds of phases are observed with similar kinetics (Figure 10.19 (b) and (d)).

Due to technical limitations, a short waiting time of about 3 minutes is introduced between the spin-coating and annealing steps and the corresponding real-time measurements. During this time, both films alter their structures to form a $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{NMP}$ structure, resembling a common intermediate complex structure for MAI-PbI_2 based compositions that can incorporate various solvent molecules,^{101,112} which is observed for the thin films in Section 9.4 based on DMF and DMSO as well. The MAPbBr_3 perovskite fraction is unchanged. Upon the start of thermal annealing, similar to the samples of other compositions discussed in the previous sections, the samples with and without thiourea start to



10.3. COMPOSITIONAL DEPENDENCE

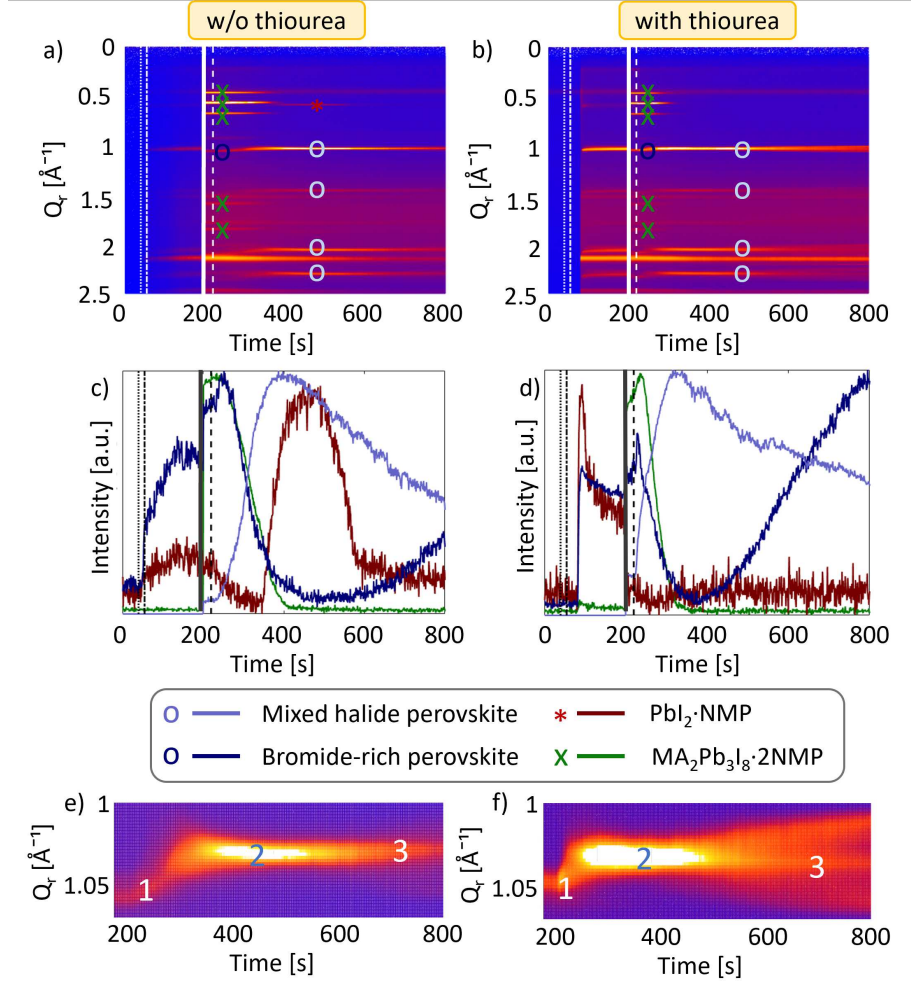


Figure 10.19: In-situ GIWAXS during thin film deposition of $\text{MAPb}(\text{I}_{0.5}\text{Br}_{0.5})_3$. (a), (c), (e) without and (b), (d), (f) with addition of thiourea. (a) and (b) Radial intensities as a function of time; (c) and (d) Integrated intensities of different crystal phases as a function of time, corresponding signature peaks for each composition can be found in Table D.3. (e) and (f) Enlarged region of the perovskite (100) signal around $q = 1 \text{ \AA}^{-1}$ from (a) and (b) during thermal annealing. Numbers mark the initial bromide-rich perovskite phase (1), the mixed perovskite phase (2) and the process of halide segregation (3). Vertical lines in (a) – (d) indicate start of spin-coating (dotted), start of gas quenching (dash-dotted), start of heating (dashed) and a 3-minute break between spin-coating and annealing (thick lines).

behave differently. While in the composition with thiourea the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{NMP}$ intermediate is converted into perovskite quickly, in the thin film without the additive, formation of the $\text{PbI}_2 \cdot \text{NMP}$ complex is observed once again while converting the iodide fraction into perovskite. This second intermediate formation does not happen when thiourea is

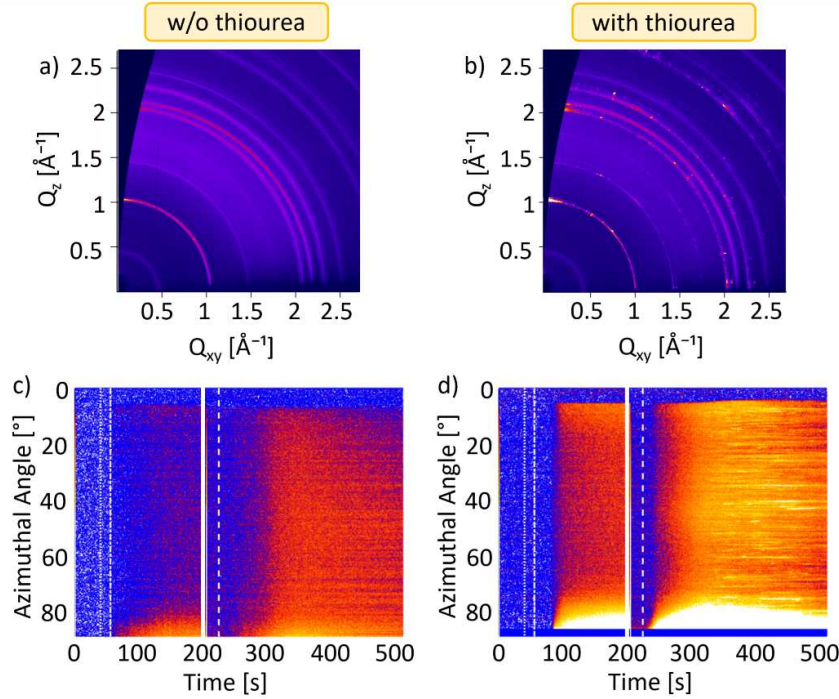
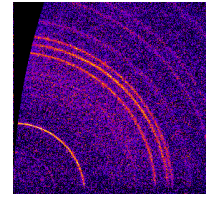
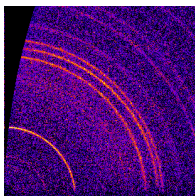


Figure 10.20: GIWAXS reciprocal space maps of $\text{MAPb}(\text{I}_{0.5}\text{Br}_{0.5})_3$ thin films (a) without and (b) with thiourea. Azimuthal intensity profiles of the (100) perovskite diffraction signal as a function of time during thin film deposition of $\text{MAPb}(\text{I}_{0.5}\text{Br}_{0.5})_3$ (c) without and (d) with thiourea, showing crystallite orientation; Vertical lines indicate start of spin-coating (dotted), start of gas quenching (dash-dotted), start of heating (dashed) and a 3-minute break between spin-coating and annealing (thick lines).

present, indicating a possible interaction of thiourea with the iodide fraction to prevent crystallization of the solvent complex in the drying thin film. Similar to previous experiments (Section 9.4), the enlarged sections in Figure 10.19 (e) and (f) visualize the gradual inclusion of iodide perovskite into the existing bromide-based perovskite structure during thermal annealing. The increase of the unit cell upon intermixing of the larger iodide into the perovskite structure is visible by a shift of the higher angle MAPbBr_3 diffraction signal (marked as 1 in Figure 10.19 (e) and (f)) to lower angles corresponding to a mixed halide perovskite material (marked as 2 in Figure 10.19 (e) and (f)). Mixing of halides seems to be slightly accelerated when the additive is present, indicating a possible effect of thiourea on ion dynamics.

The final thin films show structural properties which could be expected for mixtures of iodide and bromide-based perovskite as being a superposition of both single halide behaviors. The film without additive exhibits an intermediate grain size between the small

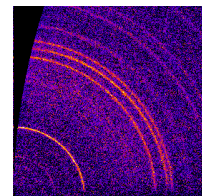


10.3. COMPOSITIONAL DEPENDENCE

MAPbI₃ crystalline grains and the larger MAPbBr₃ grains. Although a preferred orientation in the vertical direction is identified by clear angular maxima in the azimuthal GIWAXS intensity (Figure 10.20 (a)), a distinct intensity along the diffraction rings indicates a significant fraction of perovskite material with random crystallite orientation as well. This, again, is considered to be a compromise between the generally high degree of orientation of MAPbBr₃ and the tendency for random crystallite orientation for MAPbI₃. Adding thiourea increases not only the overall crystallite size, but the degree of orientation as well (Figure 10.20 (b)). This indicates its influence on the iodide fraction, which is similar to the pure MAPbI₃ composition discussed in Sections 10.1 and 10.2, inducing the growth of large, highly oriented crystallites. Consistent with the observations therein, this is found to happen during thermal annealing (see evolution of crystal orientation in Figures 10.20 (c) and (d)) and leads to a similar grain morphology of the mixed halide film as is found for the pure halide films with the addition of thiourea. Thus, thiourea causes similar morphologies of orientationally ordered, large crystallites irrespective of the halide in methylammonium-based compositions, reducing the morphological differences between MAPbBr₃ and MAPbI₃, which were observed in the pure films.

Upon prolonged thermal annealing, which was performed via irradiation with a halogen lamp, segregation of halides is observed into bromide and iodide-rich phases next to the mixed halide perovskite phase (marked by 3 in Figure 10.19 (e) and (f)). The phenomenon of halide segregation is discussed in detail in Section 9.4. Therein, a halogen lamp with a silver reflector is applied to reduce sample heating and maximize illumination. In this case, a golden reflector was employed to increase thermal radiation. Nonetheless, the illumination during thermal annealing is observed to be sufficient to trigger halide segregation. The phase segregation is found to be more pronounced for the composition with thiourea, which possibly relates to it modifying the energy landscape by increasing halide mobility.

Conclusions In summary, the observable effects of thiourea on the grain morphology of perovskite thin films depend on the material composition to a certain extent. While the strongest effect of crystalline grain enlargement and orientational ordering was observed for the MAPbI₃ material, changing the components resulted in slightly different outcomes. Changing the central cation to incorporate a FA:Cs mixture still resulted in growth of large crystallites, but no orientational order and instead a suppression of the FAPbI₃ δ -phase. Since bromide-based compositions, especially MAPbBr₃ intrinsically possess high orientational order and large crystallite size, the effects of thiourea on their growth and grain morphology were rather negligible. In halide mixtures, however, the effect of



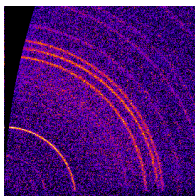
thiourea was exerted on the iodide fraction, similar to the pure iodide materials. Thus, an interaction of the thiourea with the iodide-based precursors, such as PbI_2 or MAI during the thermal annealing is plausible.

10.4 Final Remarks on the Effects of the Thiourea Additive

In synopsis of the previous three sections, adding thiourea to perovskite compositions is found to exert two distinct effects. Firstly, it induces the growth of large crystallites with diameters in the micrometer range irrespective of material composition in the final stages of deposition, i.e. during thermal annealing. This still occurs after removing part of the additive when using isopropanol as the antisolvent. Thus, a very small concentration of thiourea is already enough to induce the growth of large crystallites, possibly by altering the energetics of the perovskite material itself to modify the surface energy favoring growth of large crystallites irrespective of composition. This is considered to take place via the thiourea being present around the grain boundaries and thus, a small concentration is sufficient. The results from FTIR suggest that thiourea is coordinating the lead cations along the grain surfaces. Modifying the energy landscape by thiourea addition is consistent with the observed suppression of hexagonal phase in the FAPbI_3 -based composition as well.

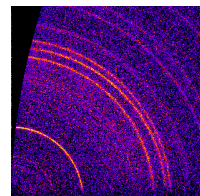
The second effect, inducing orientational order, is specific to compositions containing methylammonium and iodide. For this effect to occur, as discussed in the previous section, thiourea is required to be present in sufficient concentrations during the thermal annealing step. A possible explanation might be again related to the energetics in the material being modified by thiourea. A (110) orientational order may be energetically favorable for the MAPbI_3 composition when forming larger crystallites, while thiourea reduces the activation energy for reorientation and recrystallization, which might possibly take place via enhancement of ion mobilities. This likely requires a higher concentration of thiourea to be present during thermal annealing without it being washed away by improper antisolvents. For compositions based on other central cations such as formamidinium and cesium, this type of orientational order is potentially less favorable and thus it is not observed even with presence of thiourea. A form of interaction between thiourea and methylammonium iodide based precursors during thermal treatment cannot be excluded as well, including the possibility of chemical reaction.

These findings and speculations suggest the road to further pursue in the investigation



10.4. FINAL REMARKS

of the mechanisms of the effect of the thiourea additive, which can serve as a test case for further types of additives. An extended investigation of the complex formation in as-deposited films to elucidate the exact interactions of thiourea with the perovskite components is expected to shed more light on its working mechanisms, but for this point in time is beyond the scope of this work. Nonetheless, the presented findings provide valuable insights into the composition dependent effects of the thiourea additive on the growth and grain morphology of perovskite thin films as elucidated by in-situ GIWAXS.



Chapter 11

Structural Properties of Layered Perovskites Dictated by Spacer Cations and Perovskite Compositions

This chapter focuses on layered 2D and quasi-2D perovskite-like structures, which have been introduced in Section 2.3. Their structural variability depending on many parameters such as the spacer cation, composition and fabrication is discussed, which has been investigated by X-ray methods. In particular GIWAXS is perfectly suited for the investigation of these materials, which often exhibit a high degree of orientational order.

Simple, aromatic spacer cations are employed to form layered perovskite structures in this work. These include bifunctional molecular cations, such as 1,4-phenylenedimethylammonium (PDMA^{2+}), to form Dion-Jacobson types of structures, which are featured in Sections 11.1 and 11.2. Similar bifunctional spacer cations with different anchoring chain lengths are discussed subsequently in Section 11.3. As monofunctional molecular cations, fit for creating Ruddlesden-Popper types of layered structures, phenylethylammonium (PEA^+) and benzylammonium (BNA^+) are discussed in Section 11.4, which differ in the length of their anchoring chain as well. Finally, fluorinated PEA^+ and BNA^+ derivatives and their mixing abilities with the parent compounds are explored in Section 11.5.

The structural formulae of the investigated molecular cations are depicted in Figure 11.1. The structural variability of the resulting layered structures was investigated as a function of the spacer cation, as well as the halide counter anion and the intended stoichiometry, i.e. layer number n . For compositions targeting higher layer numbers, the small cation to form the perovskite layers was formamidinium for all presented samples, unless stated otherwise.

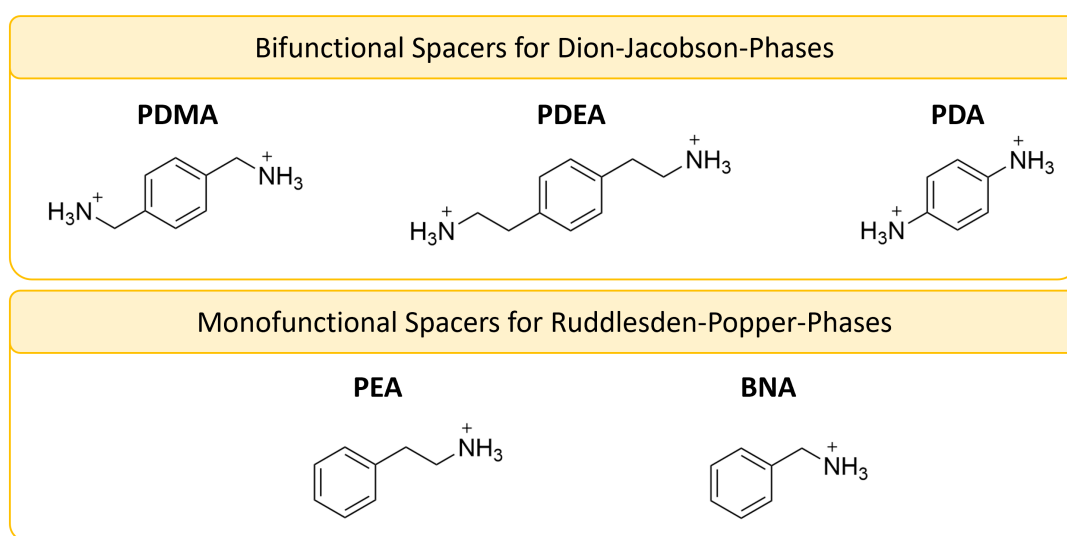
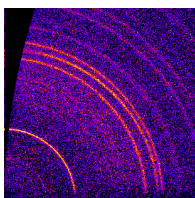
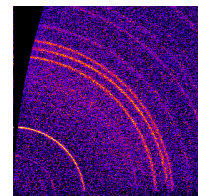


Figure 11.1: Structural formulae of the molecular spacer cations explored in layered perovskite structures in this chapter. Top row: bifunctional spacers 1,4-phenylenedimethylammonium (PDMA²⁺, IUPAC name: 1,4-phenylenedimethanaminium), 1,4-phenylenediethanaminium (PDEA²⁺, IUPAC name: 2,2'-(1,4-phenylene)diethanaminium) and 1,4-phenylenediammonium (PDA²⁺, IUPAC name: 1,4-benzenediamminium). Bottom row: phenylethanaminium (PEA⁺, IUPAC name: 2-phenylethanaminium) and benzylammonium (BNA⁺, IUPAC name: phenylmethanaminium).



11.1 Structural Complexity of Formamidinium-Based Dion-Jacobson Layered Hybrid Perovskites with the PDMA²⁺ Spacer Cation

This section is based on publication [IV]. Therein, formamidinium-based layered perovskite structures with a bifunctional spacer cation have been investigated as a function of composition. The molecular cation, 1,4-phenylenedimethylammonium (PDMA²⁺) forms layered Dion-Jacobson (DJ) types of structures⁸⁵ due to the amine moieties at both ends of the spacer. Those can interact and form hydrogen bonds with adjacent lead halide layers. As introduced in Section 3.4, DJ structures are considered more favorable for electronic applications than other types of layered perovskite structures.^{82, 262–264}

In this study, PDMA²⁺ was paired with formamidinium-based perovskite materials, and their experimental structural and optoelectronic properties compared to density func-

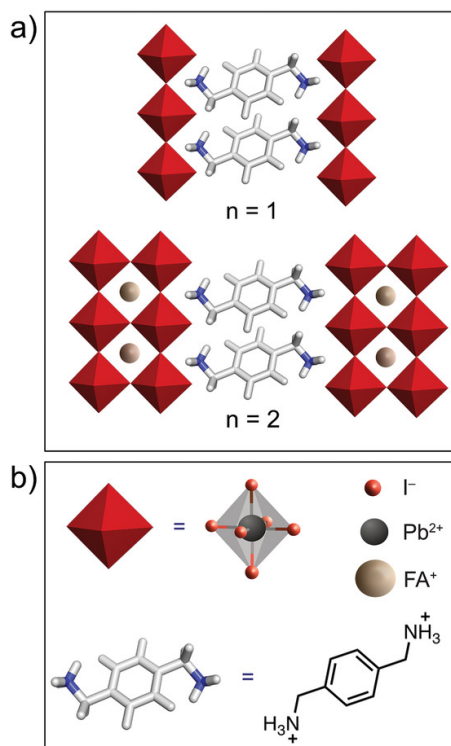
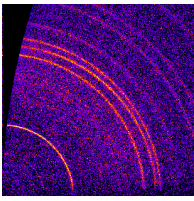


Figure 11.2: Schematic representation of Dion-Jacobson layered hybrid perovskites. (a) Envisaged structure of layered perovskites based on the $(\text{PDMA})\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ composition incorporating 1,4-phenylenedimethylammonium (PDMA²⁺) cations with (b) structural details. Image taken from publication [IV].



tional theory (DFT) calculations. While calculations suggest that with higher number n of inorganic layers, the symmetry in the inorganic layers should increase, thus creating a more perfect DJ structure, the increase of formation energies for higher n phases renders them difficult to obtain, as was confirmed in the experiment.

Orientational Order and Layer Stacking Layered perovskite thin films were prepared via spin-coating of solutions containing stoichiometric amounts of the precursors as defined by the desired target compositions of the number of inorganic layers ($\tilde{n}$). Details of sample preparation can be found in publication [IV].

In the following, $\tilde{n}$ is used to reference the target composition of the samples, while n refers to the composition of the actually detected phases. The structures of $n = 1$ and $n = 2$ phases are schematically depicted in Figure 11.2 (a), with the molecular details in Figure 11.2 (b). For the detection of low-dimensional phases, such as $n = 1$ and $n = 2$ phases, X-ray diffraction is a suitable tool due to their characteristic signals at low q -values below $q = 1 \text{ \AA}^{-1}$.⁷⁸ The XRD patterns of the thin films with $\tilde{n} = 1$ composition (Figure 11.3 (a)) exhibit such a diffraction signal at $q = 0.5 \text{ \AA}^{-1}$, which indicates the presence of a layered $n = 1$ phase. This q -value corresponds to a layer spacing of $12.4 \text{ \AA}$

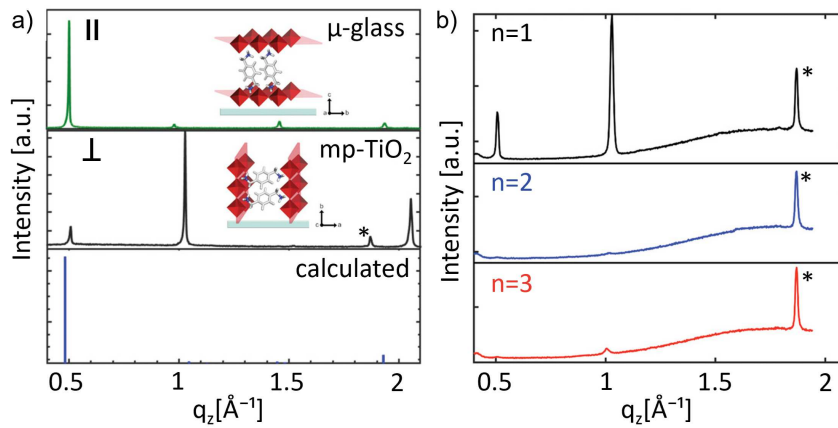
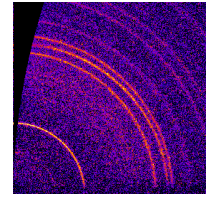


Figure 11.3: Structural properties of thin films based on $(\text{PDMA})\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ compositions. (a) Comparison of DFT-simulated (blue) with the experimental X-ray diffraction patterns of the $(\text{PDMA})\text{PbI}_4$ ($n = 1$) layered structure on either microscopical glass (green) or FTO/mp-TiO₂ (black) substrates. The inset shows schematic representations of parallel ($\parallel$) and perpendicular ($\perp$) orientations of the system with respect to the substrate, commonly associated with diffraction signals at $q_z < 1 \text{ \AA}^{-1}$ ($2\theta < 10^\circ$) and around $1 \text{ \AA}^{-1}$ (2θ around 14°), respectively. (b) X-ray reflectometry data on FTO/mp-TiO₂ substrates for $\tilde{n} = 1$ (black), $\tilde{n} = 2$ (blue) and $\tilde{n} = 3$ (red) compositions. Asterisks denote substrate peaks. Image taken from publication [IV].



for the $n = 1$ phase. The preferred orientation of the layered structure, however, can be strongly influenced by the choice of substrate. While on microscopic glass, almost exclusively parallel orientation of the perovskite layers is observed, as indicated by the strong XRD peak at $q = 0.5 \text{ \AA}^{-1}$ (Figure 11.3 (a), green curve), on a mp-TiO₂ substrate, vertical alignment of the layers is found to be preferred (Figure 11.3 (a), black curve) as indicated by the greatly reduced intensity of said peak compared to the signal at $q = 1 \text{ \AA}^{-1}$. The comparison with a calculated XRD pattern (Figure 11.3 (a), blue curve) for a parallel orientation confirms this assumption.

Comparing X-ray reflectometry (XRR) patterns for thin films with different compositions ($\tilde{n} = 1 - 3$) on mp-TiO₂ substrates (Figure 11.3 (b)), it is apparent by the low- q peak that the $\tilde{n} = 1$ sample exhibits the greatest amount of parallel oriented $n = 1$ phase, although likely a considerable proportion of vertically oriented material, indicated by the relatively high intensity of the $q = 1 \text{ \AA}^{-1}$ signal as well. Absence (or at least extreme reduction) of these signals in the reflectometry data of $\tilde{n} > 1$ samples indicates a less pronounced orientational order.

To elucidate further on the orientational order of the thin films, GIWAXS analysis was employed (Figure 11.4). Sharp diffraction spots in the reciprocal space map of the $\tilde{n} = 1$ sample (Figure 11.4 (a)) indicate crystallites with a well-defined orientational order. Both vertical and horizontal stacking are observed to be present as marked by white and black circles in Figure 11.4 (a). Additional ring-shaped intensity of the same diffraction signals indicates a considerable amount of randomly oriented crystallites.

Contrarily, the $\tilde{n} = 2$ sample exhibits only arc-shaped signals in the reciprocal space map (Figure 11.4 (b)) with maximum intensities around 45° , thus making these impossible to see in the XRR measurement, which only probes the vertical direction. This indicates that the $\tilde{n} = 2$ sample exhibits crystalline orientation preferentially along a 45° angle relative to the substrate.

In general, orientational order decreases with higher values of $\tilde{n}$ for the target composition. Hence, the reciprocal space map of the $\tilde{n} = 3$ sample (Figure 11.4 (c)) exhibits ring shaped diffraction signals with uniform angular intensity, indicative of a random orientation of crystallites with all possible stacking directions.

The degree and direction of orientational order of a layered perovskite thin film can exert a strong influence on its electronic properties and anisotropies thereof, as discussed below.

Phase Composition as a Function of Stoichiometry Besides crystallite orientation, the phase composition of the materials can be crucial for achieving the desired properties.

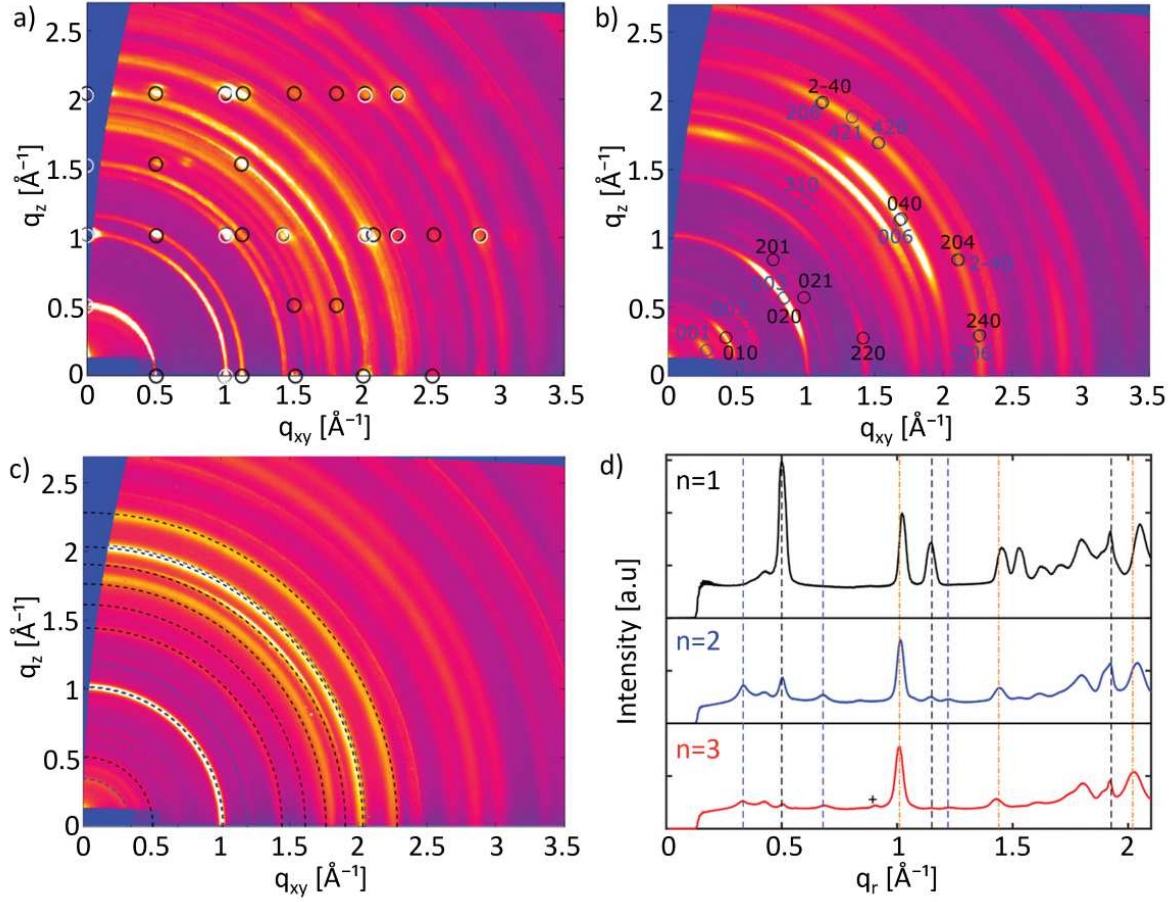
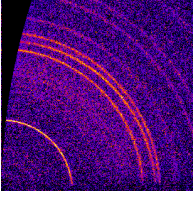
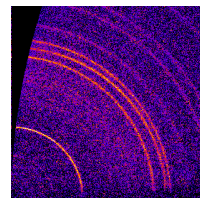


Figure 11.4: GIWAXS reciprocal space maps ($\alpha_i = 0.1^\circ$) for perovskite thin films based on $(\text{PDMA})\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ formulations with (a) $\tilde{n} = 1$, (b) $\tilde{n} = 2$ and (c) $\tilde{n} = 3$ compositions on FTO/mp-TiO₂ substrates. Spot patterns in (a) suggest well-defined orientations, while peaks from the $n = 1$ structure oriented perpendicular (parallel) to the substrate are indicated in black (white) circles. Ring-shaped features with angular maxima in (b) indicate preferred orientation, while black (blue) circles indicate layered $n = 1$ ($n = 2$) structures. Uniform angular intensity distribution in (c) is in accordance with random orientation of crystallites corresponding to $n = 1$ and $n = 2$ structures, which are indicated by black and blue dashed lines, respectively. (d) Radial intensity profiles for the reciprocal space maps in (a) – (c) for nominal $\tilde{n} = 1$ (black), $\tilde{n} = 2$ (blue) and $\tilde{n} = 3$ (red) compositions. Signals originating from distinct $n = 1$ and $n = 2$ structures are indicated by vertical dashed lines in black and blue, respectively. Yellow vertical dot-dashed lines indicate signals shared by the cubic perovskite structure, while + marks PbI₂ phase. Image taken from publication [IV].

Different layered phases can be identified by the presence of their characteristic diffraction features, best extracted from radial intensities of reciprocal space maps (Figure 11.4 (d)). The thin film with $\tilde{n} = 1$ composition exhibits a pure $n = 1$ phase, identified as already



above by the signal at $q = 0.5 \text{ \AA}^{-1}$. This $n = 1$ phase is still present in the $\tilde{n} = 2$ sample, alongside with the $n = 2$ phase, which is identified by the characteristic diffraction peaks at $q = 0.33 \text{ \AA}^{-1}$ and $q = 0.66 \text{ \AA}^{-1}$ due to the larger unit cell compared to the $n = 1$ layered structure. Thus, fabrication of the $n = 2$ phase was successful, however not phase pure. The signals of both phases are marked with black ($n = 1$) and blue ($n = 2$) markers in Figure 11.4 (b), indicating that both of them share the same angled stacking direction. In the thin film with nominal $\tilde{n} = 3$ composition, both $n = 1$ and $n = 2$ layered phases are found to be present. Their signals are marked by black ($n = 1$) and blue ($n = 2$) dashed lines in Figures 11.4 (c) and (d), indicating a small amount of these phases in the thin film alongside possibly a considerable amount of FAPbI₃ 3D perovskite, as indicated by the much higher relative intensity of the signal at $q = 1 \text{ \AA}^{-1}$, which is characteristic for perovskite structures. No indication for the presence of a $n = 3$ phase was found, which would be expected to exhibit a diffraction signal at even lower q -values than the $n = 2$ phase. Since this cannot be observed, no clear evidence for the presence of the $n = 3$ phase is found. For all samples with $\tilde{n} > 2$, a similar composition is observed, containing $n = 1$ and $n = 2$ layered phases along with α -FAPbI₃ and traces of PbI₂ phase (compare Figure D.31 in the appendix). Such a mixture of phases is in accordance with a previously reported formation of phase mixtures for $\tilde{n} > 1$ compositions of layered perovskites.^{85, 248, 442, 443}

Experimental vs Theoretically Calculated Structures Comparing the experimentally observed unit cells to the ones calculated by density functional theory (DFT, shown for $n = 1$ in Figures 11.5 and D.32 (a) and (b), appendix), they match well, with only a minor deviation of the unit cell angles from 90° due to octahedral tilting. A molecular dynamics simulation shows for the $n = 1$ phase a transition from a mixed DJ-RP structural intermediate to a pure DJ phase at temperatures above 350 K, while $n > 1$ phases persist in a DJ-like phase for all temperatures, with the unit cell angles approaching 90° with higher n for a near ideal DJ structure (compare Figure D.32 (c), appendix). This is accompanied by a widening of the octahedral cavities due to their orientation closer to 90° , allowing for a deeper penetration depth of the amine moieties of the organic spacers into the layers of inorganic lead halide octahedra and consequently a relatively smaller inter-layer distance, which is considered beneficial for the material's optoelectronic properties. A more detailed description of the methodologies and results from DFT and molecular dynamics calculations can be found in publication [IV].

The formation energies of the different layered phases, which were determined by DFT (Figure D.33, appendix), indicate that while the $n = 1$ phase is essentially thermoneutral,

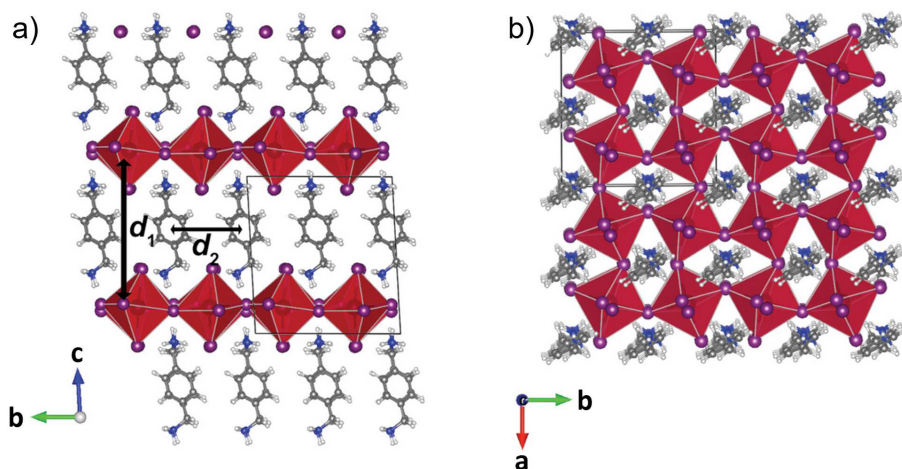
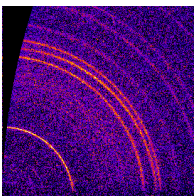


Figure 11.5: DFT-calculated structure of the $n = 1$ phase (d_1 and d_2 are the characteristic intra and inter-layer distances). Image taken from publication [IV].

with higher values of n the formation energy increases up to 0.21 eV for $n = 2$ and 0.3 eV for $n = 3$. This suggests a relative instability of the higher n phases towards the $n = 1$ and α -FAPbI₃ phases, which is consistent with experimental results, where for higher $\tilde{n}$ compositions ($\tilde{n} = 3, 4$), mainly the lower n phases ($n = 1, 2$) and the α -FAPbI₃ phase were observed.

Optoelectronic Properties Phase composition and structure of layered perovskite materials exert a strong influence on their optoelectronic properties. Thus, structural and optoelectronic investigations require to be closely linked. The absorbance spectrum of the $\tilde{n} = 1$ thin film (Figure 11.6 (a)) exhibits a single absorption peak corresponding to the $n = 1$ phase, while presence of the $n = 2$ phase can be observed by a second peak in the absorbance spectra of $\tilde{n} > 1$ samples. A large Stokes shift of the photoluminescence indicates the presence of the 3D α -FAPbI₃ phase. These results thus perfectly coincide with those obtained by X-ray diffraction.

The band gap as well as the in-plane effective carrier mass decrease with higher n , while the latter is even more decreased as compared to most Ruddlesden-Popper phases, likely due to the reduced interlayer distances of the DJ structures and the better alignment of the inorganic layers which allows for more efficient charge transport.^{82, 262–264} This reflects in increased photoconductivities for higher $\tilde{n}$ compositions (Figure 11.6 (b)). More details on the optoelectronic properties of the different thin films can be found in publication [IV] and the corresponding Supporting Information.

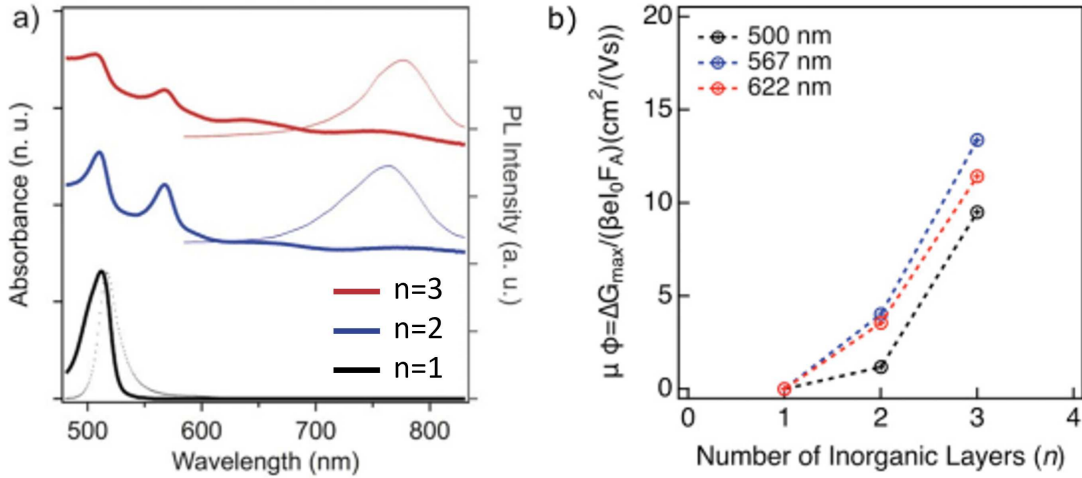
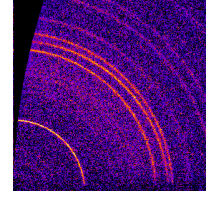
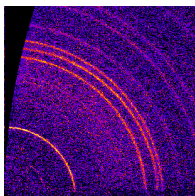


Figure 11.6: Optoelectronic properties of layered perovskite thin films. (a) UV-vis absorption (solid lines, left) and photoluminescence (PL, faded color, right) spectra of thin films based on $(\text{PDMA})\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ formulations ($\tilde{n} = 1 - 3$) on FTO/mp- Al_2O_3 substrates in accordance with previous reports.⁸⁵ (b) Maximum photoconductivity of thin films at 25 °C based on the $(\text{PDMA})\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ composition ($\tilde{n} = 1 - 3$) excited at the respective excitonic wavelengths (500, 567, and 622 nm) of $n = 1$ (black), $n = 2$ (blue) and $n = 3$ (red) phases, respectively. Image modified from publication [IV].

Conclusions It was shown that the phase composition as well as the structural and orientational order of DJ layered perovskite structures strongly depend on the stoichiometry of the precursor solution, reflecting the target dimensionality. In general, with higher $\tilde{n}$ target compositions, the orientational order is reduced and a mixture of the quasi-2D phases with $n = 1$ and $n = 2$ with 3D α -FAPbI₃ is obtained. DFT calculations confirm the relative instability of higher n phases as compared to the observed mixtures. Nonetheless, higher $\tilde{n}$ compositions show optoelectronic properties which are more favorable than their lower $\tilde{n}$ analogs, such as increased photoconductivities.

A combined study of structural analysis via GIWAXS, theoretical calculations by DFT and optoelectronic investigations allowed comprehensive characterization of the layered perovskite structures. Thus, the specific phase and ordering behavior of compositions based on the $(\text{PDMA})\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ formulation could be elucidated and rationalized as well as linked to parameters which are relevant for photovoltaic applications.



11.2 Further Parameters Influencing PDMA-based Layered Structures — Substrate, Halide Anion and Solvent

In the previous chapter, the behavior of layered perovskite materials containing the spacer cation 1,4-phenylenedimethylammonium (PDMA^{2+}) as a function of composition is elucidated. Therein, the composition was only varied in the ratios of the precursor materials PbI_2 , FAI and $(\text{PDMA})\text{I}_2$ to produce the desired $(\text{PDMA})\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ stoichiometries, but the precursor materials themselves were not altered. However, the types of materials as well as the solvents and substrates can play a role in structure formation and ordering. This section thus focuses on the effects of employing different halides (iodide and bromide), solvents and substrates for depositing thin films of layered perovskite structures with PDMA^{2+} as a spacer cation.

Although PDMA^{2+} has been promising as a spacer to form layered perovskites and stabilize perovskite-based materials for photovoltaic applications,⁸⁵ understanding its interaction mechanisms with other components of the precursor solution and the substrate is vital to choose the right compositions and parameters to fully exploit the benefits of the materials.

Influence of the Substrate $(\text{PDMA})\text{PbI}_4$ thin films were deposited on four different substrates: ITO (indium tin oxide), sapphire, quartz and mesoporous TiO_2 (m- TiO_2). Unless stated otherwise, the deposition parameters were similar to those reported in publication [IV].

GIWAXS was used to provide a quick overview over the structure formation and ordering behavior of the material on the different substrates. The reciprocal space maps in Figure 11.7 show the similarities, but distinct differences for some of the substrates as well. On ITO, sapphire and quartz, the diffraction patterns look alike, indicating the formation of a similar layered structure in a similar type of orientational order, which prefers vertical stacking of perovskite layers oriented parallel to the substrate. The radial profile (Figure 11.7 (e)) reveals slightly broader peaks for ITO and sapphire substrates, indicating a reduced degree of crystallinity. The greatest difference to the other samples is exhibited by the film on TiO_2 which, contrary to the other orientationally ordered samples, features a random crystallite orientation, as indicated by a uniform angular intensity in the reciprocal space map in Figure 11.7 (d) and visualized by the azimuthal intensity plots in Figure D.34 in the appendix as well. This is ascribed to the mesoporous nature of the surface,

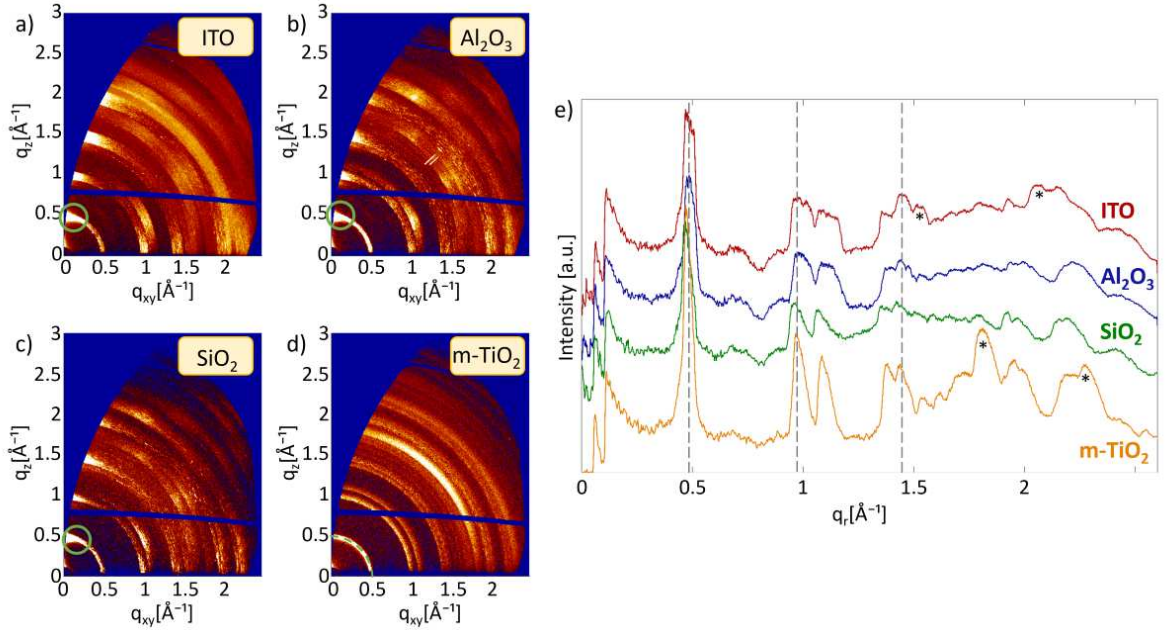
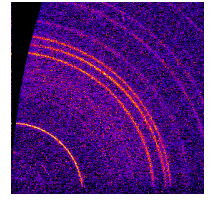


Figure 11.7: GIWAXS reciprocal space maps of $(\text{PDMA})\text{PbI}_4$ thin films on various substrates. (a) ITO, (b) sapphire, (c) quartz, (d) $m\text{-TiO}_2$. (e) Radial profiles of the reciprocal space maps in (a)–(d). Asterisks mark substrate signals. Diffraction signals used to analyze orientational order for the layered $(\text{PDMA})\text{PbI}_4$ phase are marked in green in (a–d).

which fosters intrusion of the deposited thin film material into the pores and growing random orientations depending on the pore surfaces, which is not the case on compact substrates.

Thus, the consideration of substrate choice not only has to include the electronic transport properties, which is relevant for devices, but the effects on structure formation and orientation as well, to ensure that the appropriate growth direction is supported by the substrate.

Exchanging the Halide - Iodide vs Bromide In Section 11.1, iodide-based compositions containing the PDMA^{2+} spacer cation were thoroughly investigated for their structural and optical properties. Similar to the 3D perovskite materials, in layered architectures, the choice of halide can heavily influence the structure formation and ordering behavior.^{45,444} Thus, $\tilde{n} = 1$ and $\tilde{n} = 2$ compositions of PDMA^{2+} -based layered structures using bromide as the halide anion instead of iodide were investigated by GIWAXS to reveal the distinct influence of bromide on the layered structures.

Comparing the reciprocal space maps of the bromide-based $\tilde{n} = 1$ composition (Figure

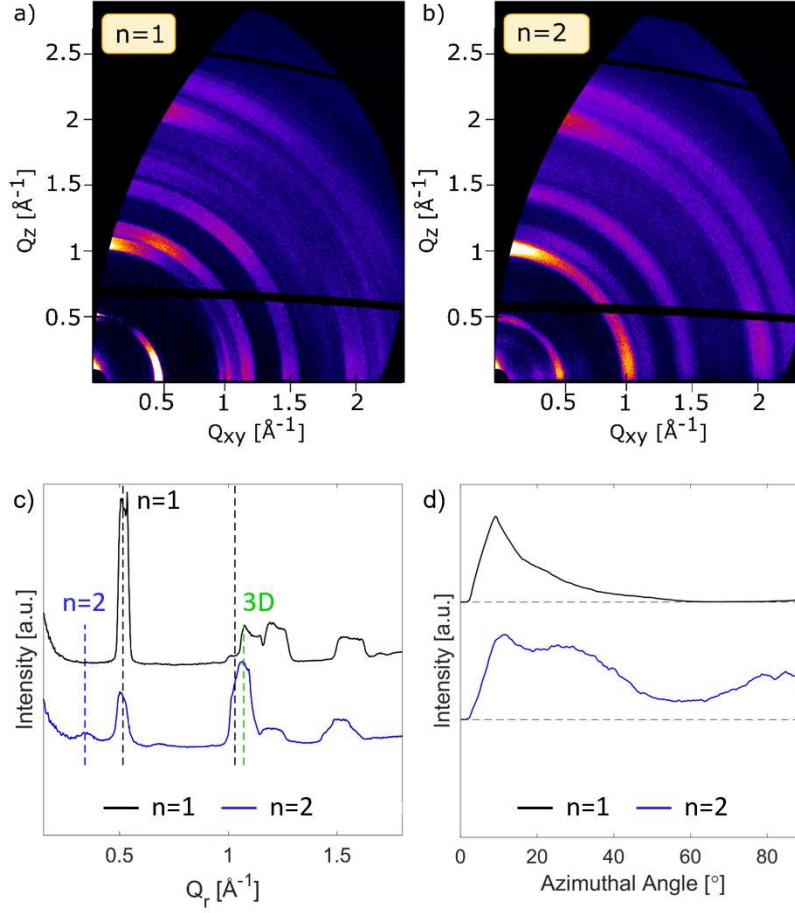
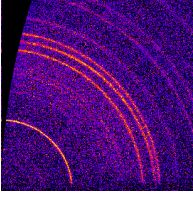
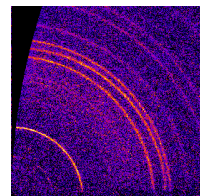


Figure 11.8: GIWAXS reciprocal space maps of (a) (PDMA)PbBr₄ ($\tilde{n} = 1$), (b) (PDMA)FAPb₂Br₇ ($\tilde{n} = 2$). (c) Radial profiles of reciprocal space maps in (a) and (b). Vertical dashed lines mark identified crystal phases. (d) Angular intensity profiles of diffraction features at $0.5 \text{ \AA}^{-1}$, ascribed to the $n = 1$ phase. Horizontal dashed lines serve as a guide to the eye.

11.8 (a)) and the iodide based analogue discussed in the previous section (Figure 11.4 (a)), it is apparent, despite both exhibiting layered structures, that their orientation relative to the substrate is distinctly different. Both compositions exhibit the layered $n = 1$ phase with preferentially ordered domains stacked in the vertical and horizontal direction. While in the iodide-based samples, the stacking direction perpendicular to the substrate (i.e. the layers aligned parallel to the substrate) is strongly favored, including bromide reverses this tendency. The stacking direction parallel to the substrate with the perovskite layers aligned perpendicular to the substrate comprises the main orientation as indicated by the intensity distribution in the diffraction signal at $q = 0.5 \text{ \AA}^{-1}$ (Figure 11.8 (a)) and



the corresponding angular intensity profile (Figure 11.8 (d), black curve).

For the $\tilde{n} = 2$ composition (Figure 11.8 (b)), the differences between the halides are even more apparent. While with iodide, $n = 1$ and $n = 2$ phase are formed in nearly equal amounts, the bromide-based material consists almost exclusively of $n = 1$ phase and 3D FAPbI_3 , while only a tiny amount of $n = 2$ phase is detected (see signal identifications in Figure 11.8 (c)). Furthermore, iodide creates a tilted main orientation of crystallites, whereas in the bromide-based thin films, the same vertical and horizontal preferred orientations are present as in the $\tilde{n} = 1$ sample. The degree of orientational order along the z -axis is reduced for the higher n composition, which is clearly illustrated by the angular intensity profiles of the same $n = 1$ phase signal at $q = 0.5 \text{ \AA}^{-1}$ (Figure 11.8 (d)).

Thus, exchanging iodide for bromide exerts a clear influence on the orientation of the layered structures, which may contain a similar mechanism as the one that induces orientational order in bromide-rich 3D perovskite thin films. Additionally, the types of structures that are formed from different precursor stoichiometries are observed to depend on the halide with bromide favoring the $n = 1$ phase. Since phase formation is a matter of energetics, this indicates different phase stabilities and phase formation energies with the different halides.

Solvent Influence Apart from the choice of halide and substrate, the solvent employed to deposit the perovskite thin films is the third major parameter which can influence structure formation and ordering behavior.^{123, 125, 416, 445} Since the most utilized solvent system for depositing perovskite thin films are mixtures of dimethylsulfoxide and dimethylformamide (DMSO:DMF, v/v) in varying ratios, this system was selected exemplary to investigate the effect of changing the solvent composition. Three different solvent compositions were employed: pure DMSO, DMF:DMSO 1:1 and DMF:DMSO 4:1, which is one of the most widely applied compositions.^{125, 445}

The reciprocal space maps of $(\text{PDMA})\text{PbI}_4$ ($\tilde{n} = 1$) thin films deposited from the three solvent mixtures (Figure 11.9 (a)–(c)) show no prominent difference between the samples, indicating that the influence of the solvent on the formation of the $n = 1$ phase is probably small. This is corroborated by the very similar radial profiles (Figure 11.9 (d)), which suggest that the same structures are formed in all films. Each film contains two main crystal orientations, one with the perovskite sheets parallel to the substrate (i.e. vertical stacking) and one tilted at around 38° .

Taking a closer look at the angular intensities (Figure 11.10 (a)) reveals a small difference in orientational order when varying the solvent mixture. To quantify the differences in orientation, the height to width ratio of the angular maxima was chosen as a measure of

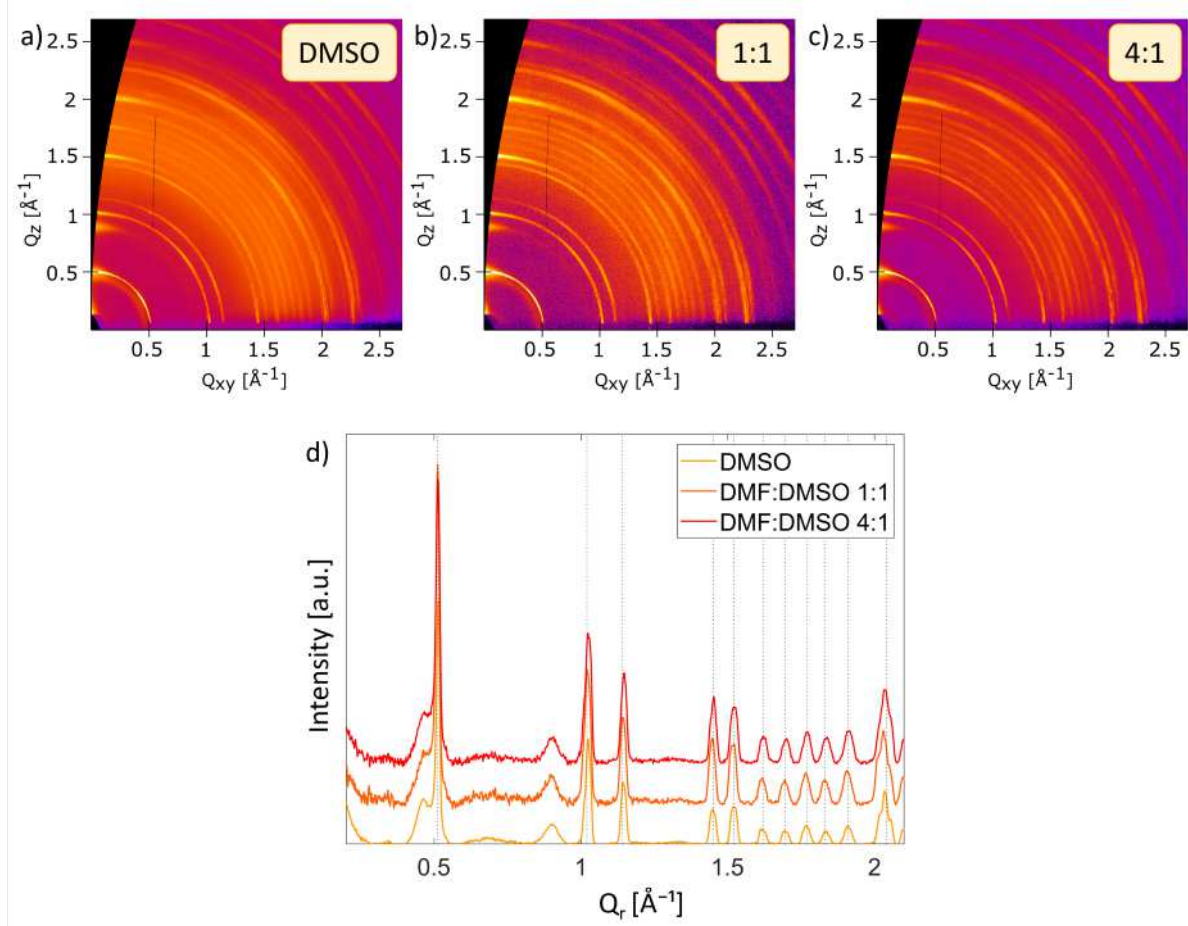
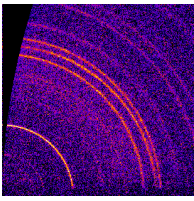


Figure 11.9: GIWAXS reciprocal space maps of $(\text{PDMA})\text{PbI}_4$ ($\tilde{n} = 1$) deposited from different solvent mixtures. (a) pure DMSO, (b) DMF:DMSO 1:1, (c) DMF:DMSO 4:1. (d) Radial profiles of reciprocal space maps in (a) – (c).

the degree of orientational order (Figure 11.10 (b)). It is observed that the overall degree of orientational order decreases with decreasing DMSO content in the solvent mixture. This occurs for both the vertical and the tilted orientation, however for the vertical orientation, the decline is halted when increasing the DMF ratio from 1:1 to 4:1, while it continues to decrease for the tilted orientation.

Thus, DMSO is found to favor orientational order in the PDMA-based layered perovskites, while an increased DMF content does not. This can be ascribed to different interaction strengths of DMSO and DMF with the precursors influencing the crystal growth, or it might likewise be related to the volatilities of the solvents with DMSO evaporating much slower and thus exerting a more structure directing role due to it staying in the film for longer. Overall, the effect of solvent is small compared to the influences of composition,

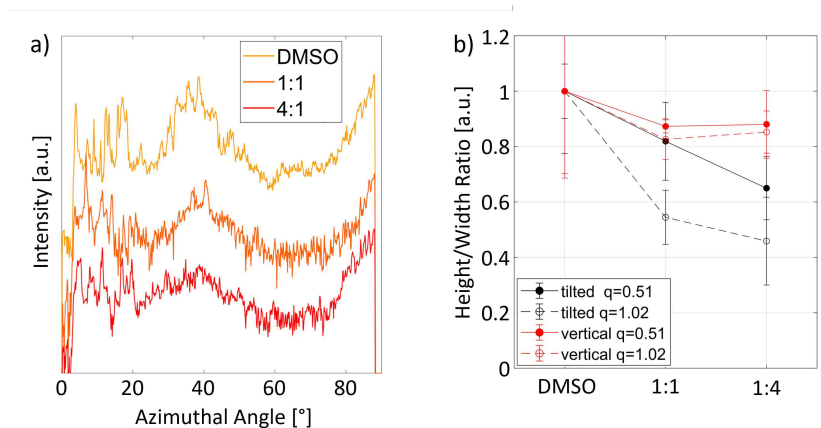
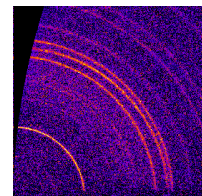
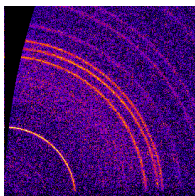


Figure 11.10: (a) Angular intensity profiles of diffraction features at $0.5 \text{ \AA}^{-1}$, ascribed to the layered $n = 1$ phase within $(\text{PDMA})\text{PbI}_4$ ($\tilde{n} = 1$) thin films deposited from different solvent mixtures. (b) Angular peak height to width ratios as a measure for the degree of orientational order.

halide anion and substrate choice. A difference in macroscopic morphology cannot be excluded, which can not be detected with the applied X-ray methodology, but would require the application of imaging techniques such as appropriate types of microscopy, which remains a subject of further research.

Conclusions Distinct influences of the material composition, especially the choice of halide, the substrate and the solvent used to deposit the layered perovskite thin films on their structural properties could be revealed by GIWAXS investigations. The strongest structure-directing effect was exhibited by the halide, which, except for the material stoichiometry, as shown in Section 11.1, is found to be mostly responsible for the establishment of orientational order and structure formation. The type of substrate is observed to play a minor role as long as the substrate is compact, while mesoporous TiO_2 induces randomly oriented growth of crystallites. Similarly, the influence of the solvent mixture when using DMF:DMSO mixtures is found to be minor compared to the effects of material composition. Further solvents were not tested and can be expected to behave differently.

In general, all investigated parameters showed a certain degree of influence on the final layered structures and require consideration when depositing perovskite thin films to receive the desired structures and optimal results.



11.3 The Role of Alkyl Chain Length and Halide Counter Ion in Layered Dion-Jacobson Perovskite Phases with Aromatic Spacers

In Section 11.1, Dion-Jacobson (DJ) layered perovskite-like structures and their properties depending on layer thickness n are discussed, while Section 11.2 reveals the influence of halide, small central cation and solvent on the structure formation. This section features DJ type layered structures as well, however the focus here is on modifying the material properties by changing the large spacer cation and the halide anion simultaneously, based on publication [V]. The stoichiometric composition $\tilde{n}$ is constant at $\tilde{n} = 1$ for all materials.

Varying the material components, especially the spacer cation for layered perovskite structures, is important for identifying compounds that can form these layered structures which exhibit suitable properties for the desired applications.^{73,75} Therefore, a systematic understanding of the structure-property relationships of such molecular cations and the materials containing them is necessary to specifically design appropriate spacer cations. These molecular spacers offer a great synthetic freedom, by adding and exchanging functional groups, the core, molecular geometry and the anchoring group. All of these require consideration when designing an organic spacer, thus knowledge of their individual influences on layered perovskite structures is crucial. This study therefore focuses on the

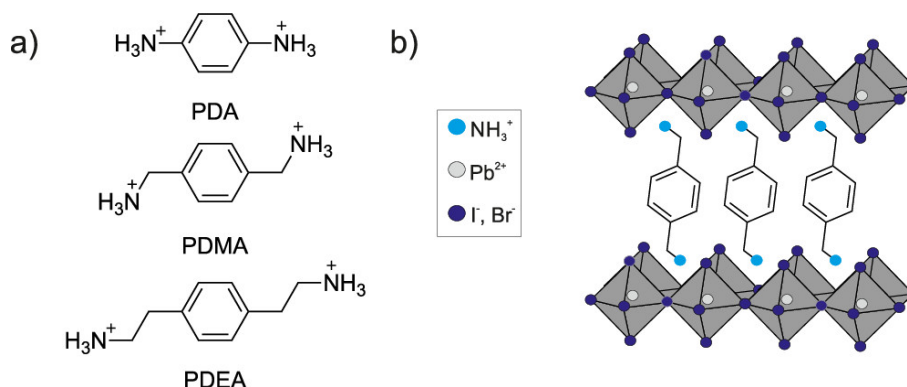
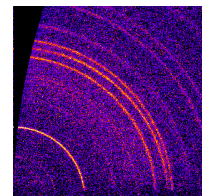


Figure 11.11: (a) Molecular structures of 1,4-phenylenediammonium (PDA^{2+}), 1,4-phenylenedimethylammonium (PDMA^{2+}), and 1,4-phenylenediethylammonium (PDEA^{2+}) organic spacers. (b) Illustration of the layered DJ perovskite structure based on a $(S)\text{PbX}_4$ composition (S indicates the bifunctional spacer cation). Image taken from publication [V].



CHAPTER 11. LAYERED STRUCTURES

effect of the anchoring group chain length, together with the counter-ions, i.e. the halides with which those anchoring groups interact.

For the spacer cation, 1,4-phenylenedimethylammonium (PDMA^{2+}) was chosen, which is discussed extensively in the previous sections. As an analogue with a longer anchoring group, 1,4-phenylenediethylammonium (PDEA^{2+}) was employed, which features one more carbon atom in the anchoring chain. In addition, 1,4-phenylenediammonium (PDA^{2+}) was employed as the shorter analogue, which does not feature any additional carbon atoms in its anchoring chain and instead has the amine moiety connected directly to the aromatic core. For molecular structures see Figure 11.11.

In general, it was found that the anchoring chain length influences not only the ability to form layered structures, but their optical properties and environmental stability as well.

Structural Variability For each of the three spacers, PDA^{2+} , PDMA^{2+} and PDEA^{2+} , thin films with compositions corresponding to $\tilde{n} = 1$ layered perovskites were deposited, while for each spacer, both iodide and bromide were investigated as counter-ions. The experimental details can be found in publication [V]. Layered perovskite structures are formed by including PDMA^{2+} and PDEA^{2+} cations, while with PDA^{2+} , the formation of 1D chain-like structures⁴⁴⁶ is found to be favored.

For both iodide and bromide-based structures, the XRD data in Figure 11.12 (a) and (b) indicate a layered structure by the distinct signal at around $2\theta = 7^\circ$. This corresponds to a q -value in the reciprocal space maps (Figure 11.12 (e) – (h)) of about $0.5 \text{ \AA}^{-1}$, where the respective signal is apparent as well. Comparing the reciprocal space maps of the PDMA-based materials (Figure 11.12 (e) and (f)) to those of the PDEA-based compounds (Figure 11.12 (g) and (h)), a much higher degree of orientational order can be observed for (PDMA) PbI_4 than for (PDEA) PbI_4 , where the layered phase is observed to consist of randomly oriented crystallites, thus showing ring-shaped diffraction signals with azimuthally homogeneous intensity. The well-ordered (PDMA) PbI_4 features clear intensity maxima along the vertical direction, suggesting a preferentially vertical stacking of layers. This difference in orientational order is reflected in the aforementioned XRD data (Figure 11.12 (a)) as well, which probes the direction vertical to the film surface in the applied thin film geometry. The red curves for (PDMA) PbI_4 show several sharp signals, while only a weak signal can be observed in the (PDEA) PbI_4 data plotted in blue since the PDEA-based structures exhibit a much greater amount of material oriented in other directions. Comparing the bromide to the iodide-based materials, the layered phase formation and the ordering trend for (PDMA) PbI_4 and (PDEA) PbI_4 is true for both halides, while for the (PDMA) PbI_4 structure (Figure 11.12 (e)), a second orientation at around

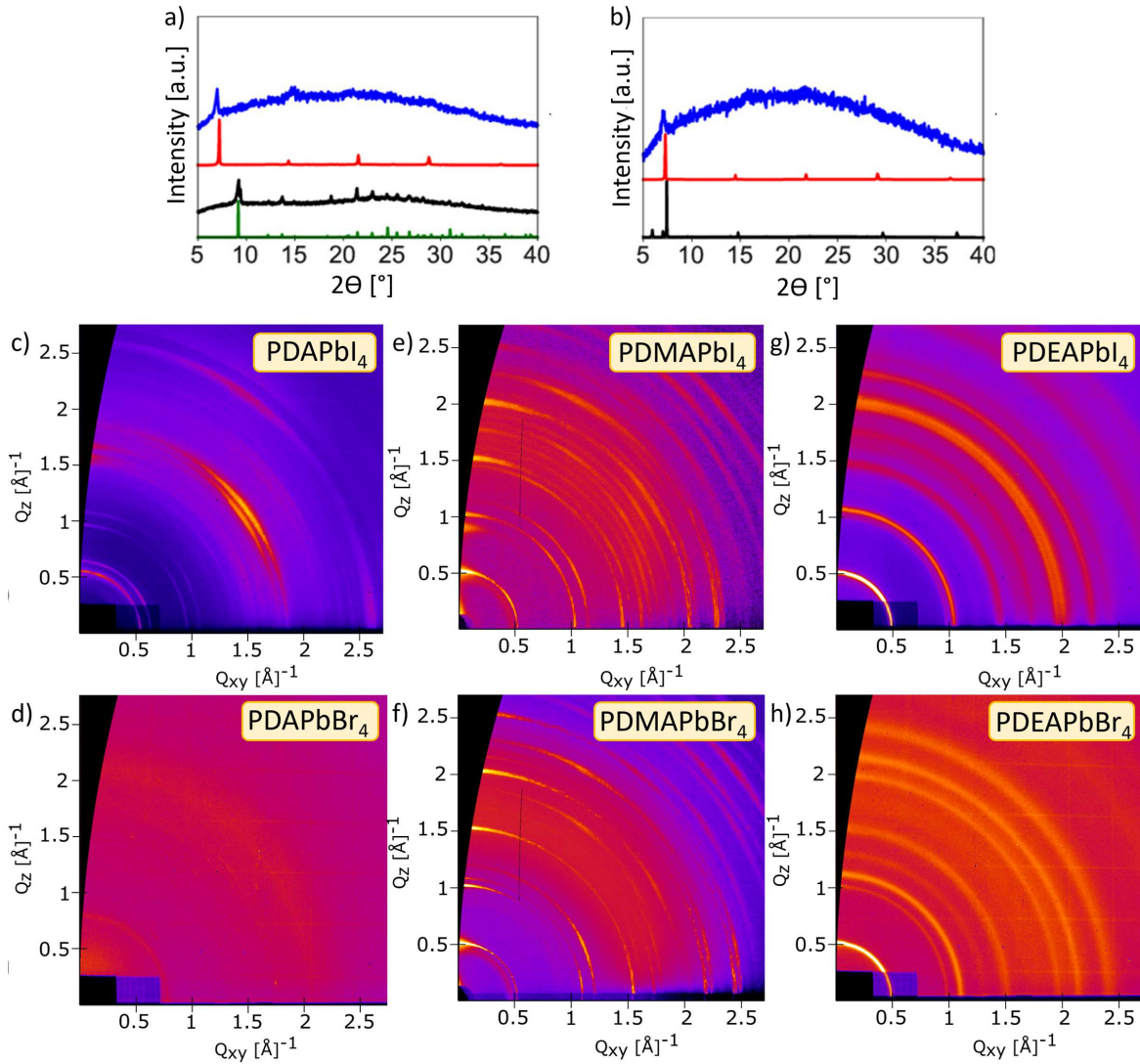
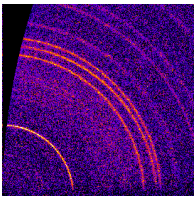
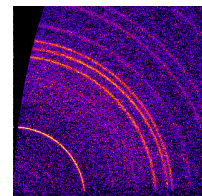


Figure 11.12: X-ray diffraction data of (a) iodide-based and (b) bromide-based $\tilde{n} = 1$ layered perovskites with different spacers: black: PDA^{2+} ; red: PDMA^{2+} ; blue: PDEA^{2+} . The green line in panel (a) shows the simulated diffractogram of $(\text{PDA})\text{PbI}_4 \cdot 2\text{H}_2\text{O}$.⁴⁴⁶ (c) – (h) GIWAXS reciprocal space maps of (c) $(\text{PDA})\text{PbI}_4$, (d) $(\text{PDA})\text{PbBr}_4$, (e) $(\text{PDMA})\text{PbI}_4$, (f) $(\text{PDMA})\text{PbBr}_4$, (g) $(\text{PDEA})\text{PbI}_4$, and (h) $(\text{PDEA})\text{PbBr}_4$. Image modified from publication [V].

30° can be found, which correlates well to the frequently observed tendency of iodide to form differently oriented layerings in perovskite materials as compared to bromides.

The differences in orientational order between PDMA-based and PDEA-based structures likely reflect a greater flexibility of the longer PDEA^{2+} spacer, which is possibly not as effective in templating a well-ordered layered structure as the more rigid PDMA^{2+} . As



CHAPTER 11. LAYERED STRUCTURES

presented in Section 11.1, when attempting to form higher n structures, compositions with the PDMA²⁺ spacer form layered structures in random orientations as well.

Contrary to the facile formation of layered perovskites with PDMA²⁺ and PDEA²⁺, the shorter PDA²⁺ spacer was found unfavorable for the formation of similar structures. The GIWAXS data for the (PDA)PbI₄ compound (Figure 11.12 (c)), compared to those from PDMA²⁺ and PDEA²⁺, indicates formation of a similar layered phase. Meanwhile, the deviating signals found in XRD (Figure 11.12 (a), black curve) were matched with a previously reported (PDA)PbI₄·2H₂O dihydrate structure,⁴⁴⁶ featuring a one-dimensional arrangement of chains of lead-halide octahedra. (PDA)PbI₄ thus is considered to be prone to hydration. This behavior can likely be explained by the lack of flexibility of the short anchoring chains of PDA²⁺, which only allow a rather low penetration depth into the perovskite layers, likely rendering it vulnerable towards hydration. Additionally, PDA²⁺ was found to be unstable in solution and degraded over time (see Supporting Information of publication [V]). Replacing iodide by the smaller bromide is observed to at least enable formation of layered structures from fresh solutions, as indicated by the signals in the X-ray diffractogram (Figure 11.12 (b)). Additional signals at low diffraction angles indicate formation of a corrugated structure, which has been observed in other compositions before.^{447,448} Note that the GIWAXS data in Figure 11.12 (d) represents a sample fabricated from an aged solution and thus lacks a clearly ordered structure. These findings show that PDA²⁺ and its corresponding layered structures are relatively unstable towards degradation and hydration, making the fabrication of layered perovskites challenging and hardly reproducible.

Optical Properties The variation in anchoring chain length and counter-ion not only influences the structure but along with it the optical properties of the resulting thin films. Increasing the molecular length likewise increases the size of the unit cell in the crystal structure and thus the potential barrier width.^{237,255} This is reflected in the absorption spectra of PDMA and PDEA-bromide and iodide-based layered perovskite structures, shown in Figure 11.13 (a) and (c). An absorption maximum around 500 nm for iodide compounds is typical for a layered perovskite material,⁴⁴⁹ while the slight shift to lower wavelengths with increasing molecular length indicates an increase in the band gap due to a slightly larger interlayer distance. The bromide compounds in general possess wider band gaps than their iodide counterparts, thus all absorption is shifted to higher energies (shorter wavelengths), but the behavior upon varying the spacer cation is retained. The PDA-based materials show broad absorption at higher energies, which can be attributed to the formation of the chain-like structures.⁴⁵⁰

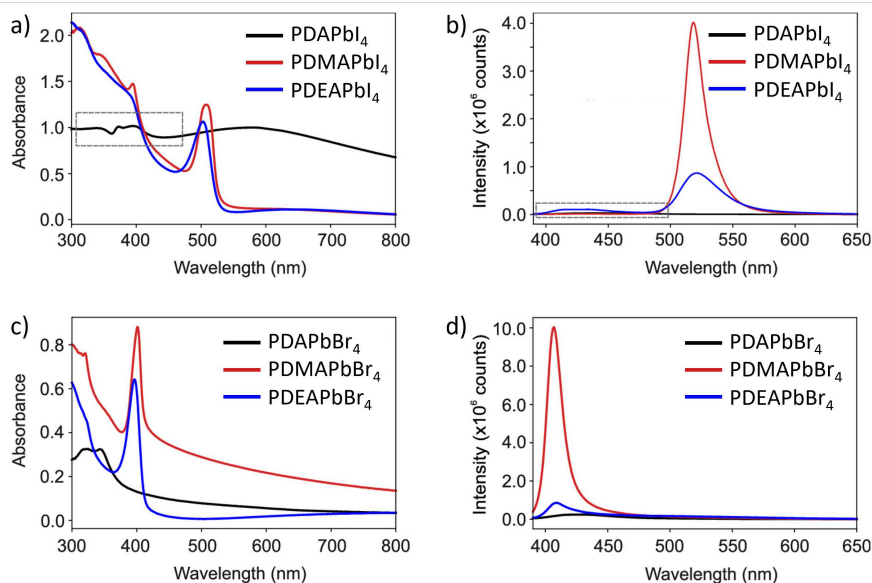
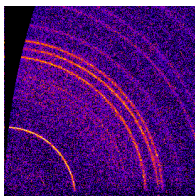


Figure 11.13: (a) UV-vis absorption and (b) steady state photoluminescence (PL) emission spectra of (PDA)PbI₄ (black), (PDMA)PbI₄ (red), and (PDEA)PbI₄ (blue). (c) UV-vis absorption and (d) steady-state PL emission spectra of (PDA)PbBr₄ (black), (PDMA)PbBr₄ (red), and (PDEA)PbBr₄ (blue). Image adjusted from publication [V].

Comparing the emission spectra (Figure 11.13 (b) and (d)) to the absorption spectra, clear emission maxima can be seen for both the PDMA and PDEA-based compounds. A slightly larger Stokes shift and an increased peak width can be observed for (PDEA)PbX₄. This could be related to the greater structural disorder associated with the longer anchoring chain or an increased vibrational relaxation of the larger molecular cation.⁴⁴⁷ A more detailed analysis of the optical properties of the investigated materials can be found in publication [V].

Environmental Stability To assess the environmental stability of the materials, the thin films were exposed to a humid atmosphere of 70 % relative humidity, while the structural alterations were examined by XRD (Figure 11.14).

For the PDA-based materials, the iodide compound did not show any changes upon humidity exposure, due to the fact that it had been already hydrated before (Figure 11.14 (a)). The bromide-based structure, however, showed distinct alterations and the emergence of new signals, which can be possibly ascribed to hydrated structures (Figure 11.14 (d)). Thus, even though with bromide, the PDA²⁺ layered structure is slightly more stable than with iodide, under high humidity both of them are prone to hydration.

A clear stabilizing effect of bromide against hydration can be seen in the PDMA-based

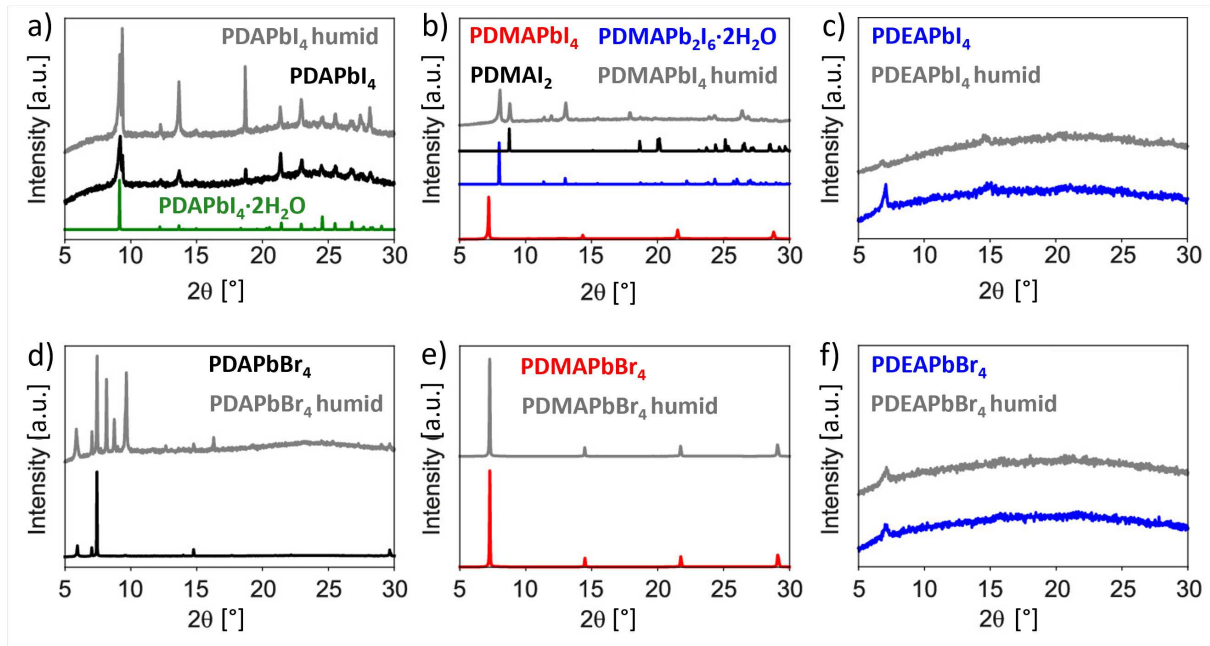
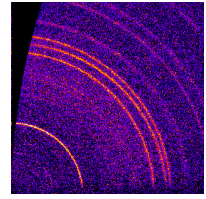
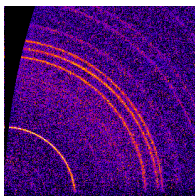


Figure 11.14: X-ray diffractograms of (a) pristine (black) and hydrated (gray) (PDA)PbI₄ films and the calculated pattern for (PDA)PbI₄·2H₂O (green);⁴⁴⁶ (b) pristine (red) and hydrated (gray) (PDMA)PbI₄ films, and the calculated patterns for (PDMA)Pb₂I₆·2H₂O (blue) and (PDMA)I₂ (black);⁴⁵¹ (c) pristine (blue) and humidity-treated (gray) (PDEA)PbI₄ films. Diffraction patterns of Br-based samples employing PDA²⁺, PDMA²⁺ and PDEA²⁺ spacers are shown in panels (d), (e) and (f), respectively. Image taken from publication [V].

materials (Figure 11.14 (b) and (e)). The bromide-based (PDMA)PbBr₄ layered material is stable in the humid atmosphere and does not show any signs of structural degradation, while the iodide-based material hydrates within minutes. A hydrated phase as well as possible formation of (PDMA)I₂ were identified, indicating degradation of the material. This stabilizing effect of bromide against hydration may be attributed to a contracted lattice due to the smaller bromide ion, hindering water intercalation, or stronger interactions between bromide and the spacers.

The structures containing the larger PDEA²⁺ spacer, are found to be stable against hydration independent of the counter-ion, as for both thin films, no significant changes were observed in the XRD patterns before and after humidity exposure (Figure 11.14 (c) and (f)). This is attributed to the increased hydrophobicity of the larger organic cation.

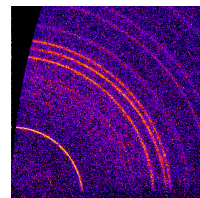
The corresponding findings in the optical properties upon humidity exposure, corroborating the results from XRD analysis, can be found in publication [V].



Conclusions This section has shown how the formation and material properties of layered perovskites can be influenced by the choice of halide and the anchoring chain length as one specific property of the spacer. The chain length dictates the ability to form layered phases as well as the degree of orientational ordering in those phases and exerts a fine influence on the optical properties. These are, however much stronger influenced by the choice of halide, while for the structure formation and degree of order, the role of the halide is subordinate as compared to the influence of the chain length. Material stability, on the other hand, is achieved by an interplay of the beneficial effects of bromide inclusion and longer spacer cations with higher hydrophobicity.

This investigation serves as an example how small variations in the molecular structure of the organic spacer cation can drastically influence the final layered structure and offers insights for a systematic design of spacers. Considering parameters such as molecular flexibility, size and the possibility of the anchoring moieties to intrude into the voids of the inorganic layer will be vital for efficient design of spacers.

Once more, X-ray diffraction served as a valuable tool to reveal the distinct structure formation, ordering and degradation behavior of each composition. In combination with optical analysis, important structure-property relationships, which are of relevance for potential applications could be elucidated.



11.4 BNA⁺ and PEA⁺ for Ruddlesden-Popper Phases and Perovskite Phase Stabilization

Moving on from the Dion-Jacobson type of structures in the previous two sections, this section focuses on the second major structural type of layered perovskite structures, the Ruddlesden-Popper (RP) phases.^{78–81} As introduced in Section 2.3, these require a monovalent spacer cation to form a bilayer of organic spacers between the inorganic lead halide layers. Part of this section is based on publication [VI], which discusses the introduction of small amounts of the spacer cation benzylammonium (BNA⁺) into a FAPbI₃ perovskite film. The formation of layered phases is shown by samples with $\tilde{n} = 1$ and $\tilde{n} = 2$ compositions and their possible presence in the BNA-modified samples as well as the effect on the perovskite material is discussed. Finally, these results are compared to the ones employing phenylethylammonium (PEA⁺) cations as an analog to BNA⁺ with a longer anchoring chain containing one more carbon atom. Both BNA⁺ and PEA⁺ are shown to form layered phases of $n = 1$ and $n = 2$ stoichiometry with FA⁺ as the small cation and iodide as the counter anion.

Layered Benzylammonium Compositions The GIWAXS reciprocal space maps of BNA-based $\tilde{n} = 1 - 3$ compositions (Figure 11.15 (a)–(c)) reveal the formation of well-ordered layered phases as indicated by the low- q diffraction signals around $0.5 \text{ \AA}^{-1}$ and below. In the corresponding radial profiles (Figure 11.15 (e)), the signals ascribed to distinct crystal phases are labeled, revealing a preferred formation of $n = 2$ phase in the $\tilde{n} > 1$ samples relative to the $n = 1$ phase. Even in the $\tilde{n} = 1$ sample, the intensity of $n = 1$ phase is rather low, which indicates a reduced stability of the $n = 1$ phase under these conditions, at least relative to the $n = 2$ phase, which is found to be almost phase pure in the $\tilde{n} = 2$ sample with only very small amounts of $n = 1$ phase. Similarly, the $\tilde{n} = 3$ sample features only a small amount of $n = 2$ phase next to the 3D perovskite phase, with no detectable amount of $n = 1$ phase, again indicating preferred formation of the $n = 2$ phase. A small amount of PbI₂ is present in all $\tilde{n} = 1 - 3$ samples, which might be related to phase segregation or even a general tendency of BNA⁺ to phase segregate from the PbI₂ instead of forming low dimensional phases.

Notably, these samples have been annealed at high temperatures (150 °C) for an extended period of time (30–40 min, more details concerning sample fabrication can be found in publication [VI]). This is commonly applied to convert FAPbI₃ into the perovskite phase since it otherwise tends to form the non-perovskite δ -phase,^{35,87,380,381} but in most cases

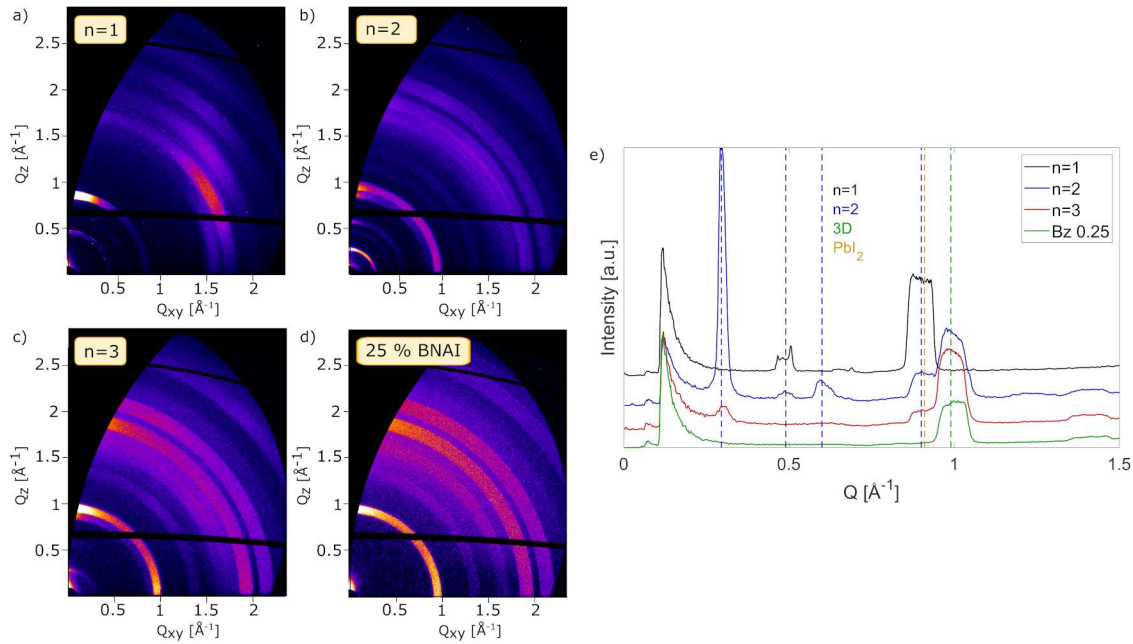
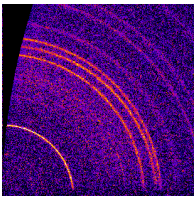


Figure 11.15: GIWAXS reciprocal space maps of layered benzylammonium-based samples with different compositions of the $(\text{BNA})_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ formulation. (a) $\tilde{n} = 1$, (b) $\tilde{n} = 2$, (c) $\tilde{n} = 3$, (d) 25 % (BNA)I mixed into a FAPbI_3 -based perovskite composition. (e) Radial profiles of the reciprocal space maps in (a)–(d). Image modified from publication [VI].

not required for low-dimensional structures.⁷⁵ Thus, a series of samples was produced without annealing, but otherwise similar fabrication parameters and compositions. The corresponding reciprocal space maps in Figure 11.16 (a)–(c) indicate the formation of low dimensional $n = 1$ and $n = 2$ phases already without annealing. The $\tilde{n} = 1$ sample produced a very grainy diffraction pattern (Figure 11.16 (a)), suggesting either a low coverage film or singular, larger crystallites. The peak positions, marked in the respective radial profile (Figure 11.16 (e)) reveal indeed an almost phase pure $n = 1$ material. Consequently, the low intensity and strong PbI_2 presence in the annealed sample likely results from thermal degradation during annealing.

Analogous to the annealed samples, the $\tilde{n} = 2$ and $\tilde{n} = 3$ compositions (Figure 11.16 (b), (c) and (e)) exhibit preferred formation of the $n = 2$ layered phase with only a tiny amount of $n = 1$ phase. Excess FAPbI_3 phase can be observed as well, which due to the missing heat treatment adopts the δ -phase.

Similar to the DJ phases in Section 11.1, for the BNA-based RP phases, the predominant crystal orientation depends on the stoichiometry of the precursor solution. The

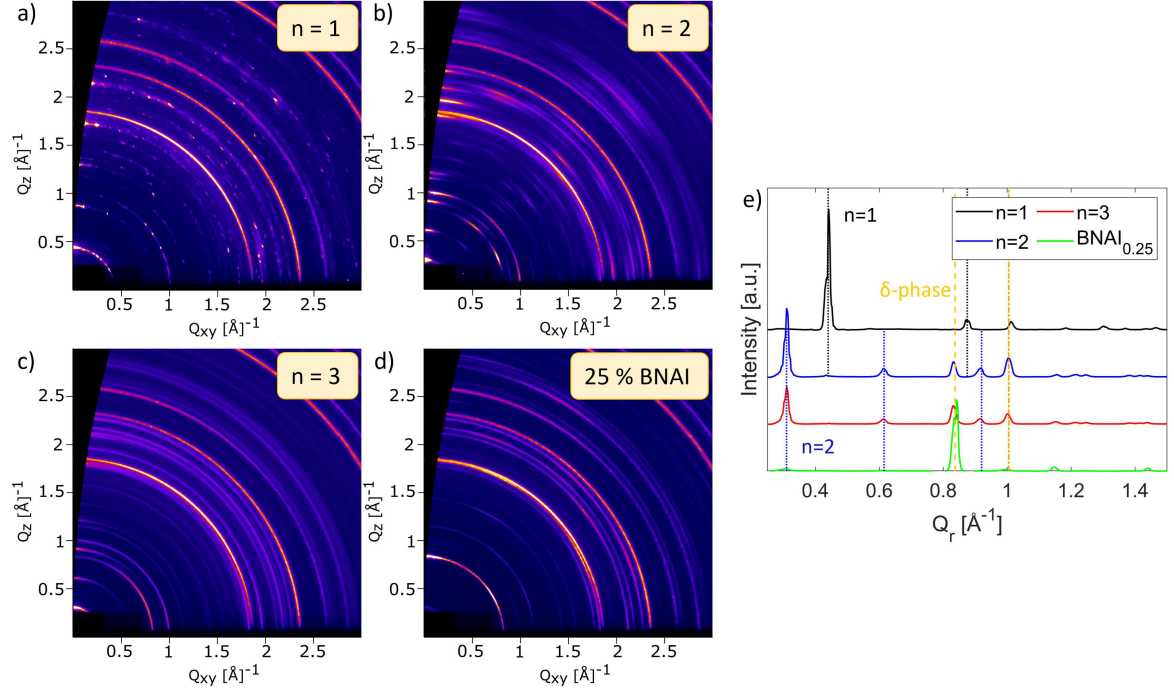


Figure 11.16: GIWAXS reciprocal space maps of layered benzylammonium-based samples without thermal annealing, containing different compositions based on the $(\text{BNA})_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ formulation. (a) $\tilde{n} = 1$, (b) $\tilde{n} = 2$, (c) $\tilde{n} = 3$, (d) 25 % (BNA)I mixed into a FAPbI_3 -based perovskite. (e) Radial profiles of reciprocal space maps in (a)–(d). Compositions in the legend give nominal compositions $\tilde{n}$, while vertical lines indicate identified crystal phases. Black dotted from the top: $n = 1$ phase; blue dotted from the bottom: $n = 2$ phase; yellow dashed: FAPbI_3 δ -phase; orange dot-dashed: Peak shared by $n = 1$, $n = 2$ and FAPbI_3 α -phase.

degree of orientational order decreases with increase of $\tilde{n}$ in the composition, in both the as-deposited (Figure 11.16) and annealed (Figure 11.15) samples as seen by the distinct intensity distributions of the diffraction rings. For the $\tilde{n} = 1$ composition, one main orientation is present, while for $\tilde{n} = 2$ several preferred orientations coexist and $\tilde{n} = 3$ exhibits a much higher ratio of randomly oriented material.

Another factor that has shown to influence structure formation and orientational ordering for the DJ phases in Section 11.2 is the type(s) of ions employed to form the layered perovskite structure, especially the halide, but the small central cation as well. Thus, additional samples with a BNA-based $\tilde{n} = 3$ composition were prepared featuring either iodide or bromide as the halide anion and a mix of 95 % FA^+ and 5 % Cs^+ as the small central cation.

Adding cesium cations to the mixture is observed to indeed affect the structure of the

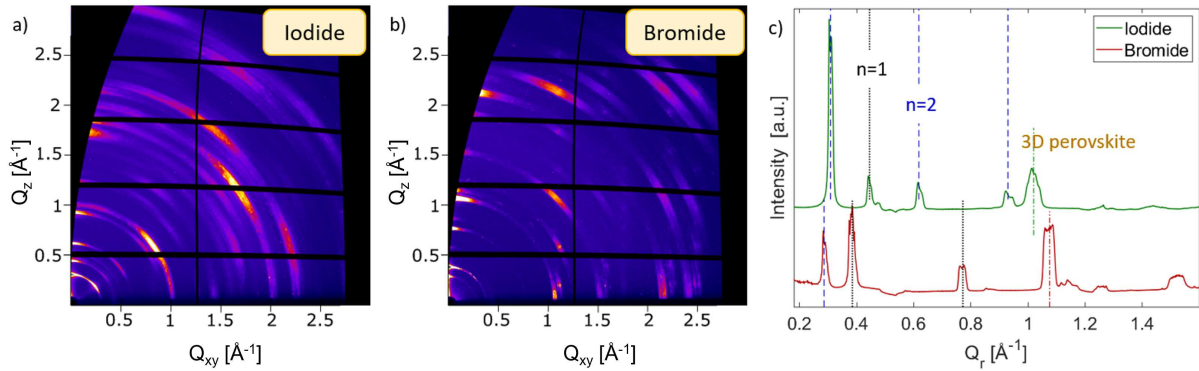
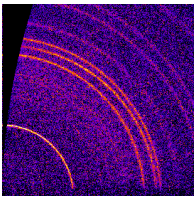
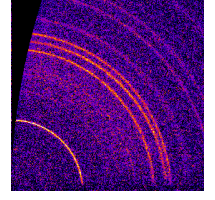


Figure 11.17: GIWAXS reciprocal space maps of layered benzylammonium-based samples with $(\text{BNA})_2(\text{FA}_{0.95}\text{Cs}_{0.05})_2\text{Pb}_3\text{X}_{10}$ ($\tilde{n} = 3$) composition (a) $\text{X}=\text{I}$, (b) $\text{X}=\text{Br}$. (c) Radial profiles of reciprocal space maps in (a) and (b).

iodide-based sample. Comparing the corresponding reciprocal space map in Figure 11.17 (a) to the sample based solely on formamidinium (Figure 11.16 (c)), it is apparent that the crystal orientation is altered: while in the FA^+ -based sample, the vertical and horizontal orientations both are found to be equally preferential, with the addition of cesium a tilted orientation is adopted as can be seen from the intensity maxima along the main ring-shaped diffraction signals. Similar to the FA^+ -based sample, the $\tilde{n} = 3$ composition mainly forms the $n = 2$ phase as a layered perovskite phase, together with a smaller amount of 3D $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$, but here a considerable amount of $n = 1$ phase is found as well.

The strong effect of bromide on the crystallite orientation, which was observed in 3D perovskite materials (Section 9.4) as well as in DJ phases (Section 11.2) is likewise apparent in the BNA-based RP phases. Retaining all further parameters and components and only replacing iodide with bromide results in a highly oriented layered system with pronounced vertical stacking, as indicated by the spot-like diffraction pattern in the reciprocal space map (Figure 11.17 (b)). Furthermore, the bromide-based sample contains a significantly greater proportion of $n = 1$ phase relative to the $n = 2$ phase than the iodide-based sample, which is visible in the radial profiles in Figure 11.17 (c). A similar trend of preferring the $n = 1$ phase with bromide was observed for the PDMA^{2+} spacer, indicating a similar mechanism of bromide stabilizing the $n = 1$ phase.

Comparable effects of bromide substitution on BNA-based layered RP phases can be observed on samples based on pure formamidinium as well (Figure D.35, appendix), which tend to exhibit a more pronounced vertical ordering and a higher proportion of $n = 1$ phase when employing bromide instead of iodide. This is an indication that the mech-



anisms of bromide inducing crystallite orientation and favoring of the $n = 1$ phase are universal and not limited to the spacer cation or certain small cation compositions. The higher binding strength of bromide to the lead cation potentially plays a role in this, as well as the smaller ion size.

Layered Phenylethylammonium (PEA^+) Compositions To compare the layered systems based on BNA^+ to the more widely used PEA^+ spacer, samples were produced with similar compositions and fabrication parameters (found in publication [VI]), except for the replacement of $(\text{BNA})\text{I}$ by $(\text{PEA})\text{I}$. The reciprocal space map for the $(\text{PEA})_2\text{PbI}_4$ $\tilde{n} = 1$ composition in Figure 11.18 (a) reveals an extremely well ordered, phase pure layered $n = 1$ phase, which is found to exhibit a double stacking of distinguishable unit cells,²⁶¹ as indicated by the doubled amount of diffraction spots in the vertical scattering rods.

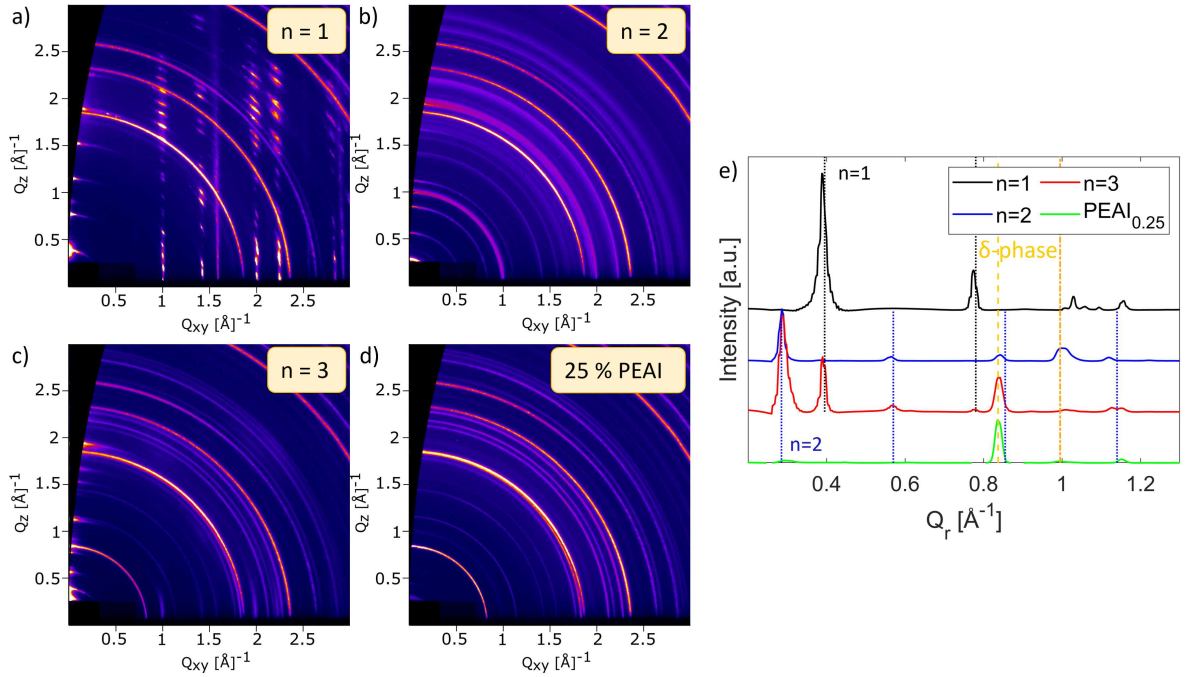
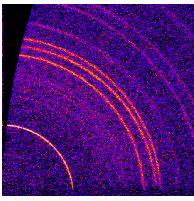


Figure 11.18: GIWAXS reciprocal space maps of layered phenylethylammonium (PEA^+) based samples without thermal annealing, containing different compositions based on the $(\text{PEA})_2\text{FA}_{n-1}\text{Pb}_n\text{I}_{3n+1}$ formulation. (a) $\tilde{n} = 1$, (b) $\tilde{n} = 2$, (c) $\tilde{n} = 3$, (d) 25 % $(\text{PEA})\text{I}$ mixed into a FAPbI_3 -based perovskite composition. (e) Radial profiles of reciprocal space maps in (a) – (d). Compositions in the legend give nominal compositions $\tilde{n}$, while vertical lines indicate identified crystal phases. Black dotted from the top: $n = 1$ phase; blue dotted from the bottom: $n = 2$ phase; yellow dashed: FAPbI_3 δ -phase; orange dot-dashed: Peak shared by $n = 1$, $n = 2$ and FAPbI_3 α -phase.



Adding formamidinium for an $\tilde{n} = 2$ composition (Figure 11.18 (b)) results in formation of an almost pure $n = 2$ phase with only minor amounts of FAPbI₃ δ -phase present. Upon increase of the FA⁺ concentration for an $\tilde{n} = 3$ composition (Figure 11.18 (c)), the sample is observed to contain both $n = 1$ and $n = 2$ phases as well as a small amount of FAPbI₃ δ -phase. The occurrence of the $n = 1$ phase in higher $\tilde{n}$ PEA-based thin films, which was not observed for the BNA-based samples, suggests a higher relative stability of the $n = 1$ phase when incorporating PEA⁺ as compared to BNA⁺.

The trend of decreasing orientational order with increasing $\tilde{n}$ holds only for $\tilde{n} = 1$ and $\tilde{n} = 2$ with PEA⁺, since the degree of orientation is observed to be much lower for the $\tilde{n} = 2$ thin film, resulting in circularly extended diffraction signals. In the $\tilde{n} = 3$ sample, however, the layered phase is found to exhibit a much higher orientational order than in

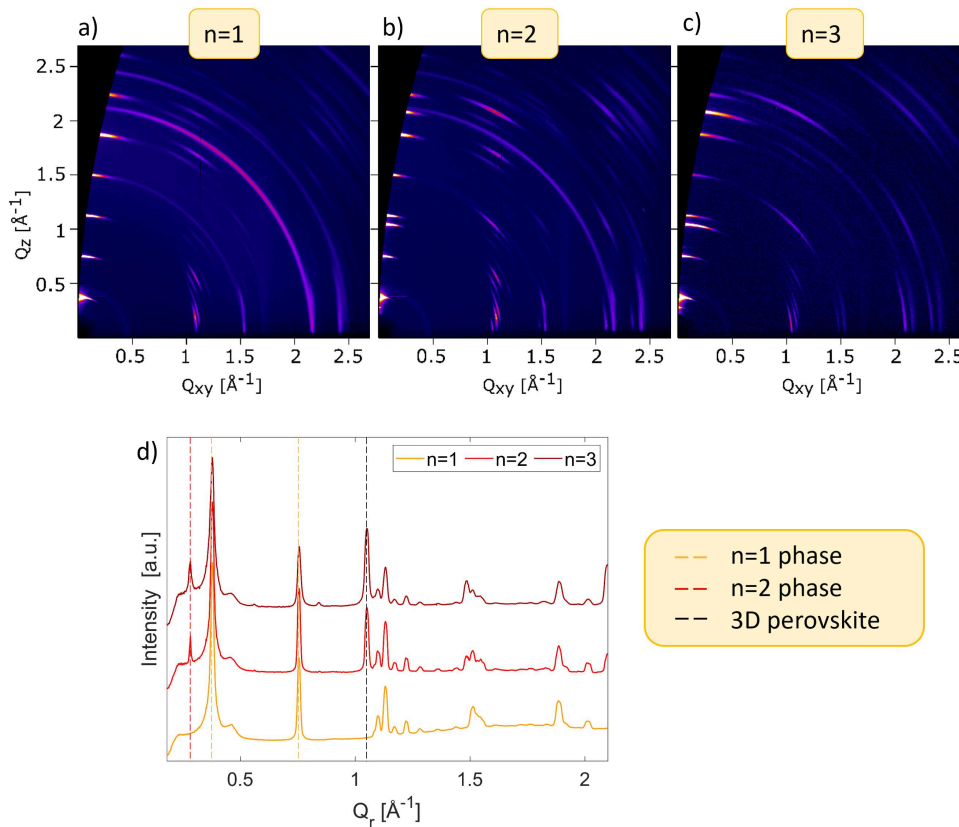
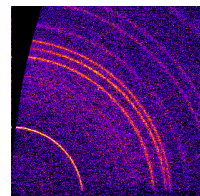


Figure 11.19: (a)–(c) GIWAXS reciprocal space maps of bromide-based layered perovskite thin films with phenylethylammonium spacers with different compositions based on the $(\text{PEA})_2\text{FA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ formulation. (a) $\tilde{n} = 1$, (b) $\tilde{n} = 2$, (c) $\tilde{n} = 3$, (d) Radial profiles of reciprocal space maps in (a)–(c). Vertical lines indicate distinct crystal phases as stated in the legend.



the $\tilde{n} = 2$ material, as indicated by the extended series of sharp diffraction spots along the q_z -axis. This increased amount of orientational order for the $\tilde{n} = 3$ composition is potentially related to the presence of the $n = 1$ phase, which due to its tendency for high orientational order, likely induces this orientational order in the $\tilde{n} = 3$ composition as well.

Therefore, the major difference between the otherwise similar behavior of PEA^+ and BNA^+ in the formation of layered perovskite phases is the $n = 1$ phase, which is found to be favored more relative to other phases when using PEA^+ rather than BNA^+ , while the $n = 2$ phase still dominates the higher $\tilde{n}$ PEA-iodide compositions. PEA-based layered phases, especially the $n = 1$ phase, exhibit a very high amount of orientational order, including a double stacking of distinguishable unit cells, while $(\text{BNA})_2\text{PbI}_4$ tends to even form several different polymorphs of the layered phase, as described in the next section, which could be a hint to explain the differences in observed stability as well.

Replacing iodide in PEA-based layered structures by bromide to create compositions of $(\text{PEA})_2\text{FA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ with $\tilde{n} = 1 - 3$ is observed to alter the relative phase stabilities and thus the phase composition of thin films as well. In the radial profiles (Figure 11.19 (d)) of the reciprocal space maps (Figure 11.19 (a) – (c)) of PEA-bromide based thin films, a preference of the $n = 1$ phase in higher $\tilde{n}$ samples can be observed, with only a minor amount of $n = 2$ phase present. This is similar to the BNA-bromide based compositions, where an increase of the amount of $n = 1$ phase was observed when substituting bromide as well. Generally, the bromide-based samples all feature a high degree of orientational order, and the phase composition of higher $\tilde{n}$ samples is very similar with an increasing amount of $\alpha\text{-FAPbI}_3$ when increasing $\tilde{n}$.

It has to be noted that all these investigations and findings rely on formamidinium-based materials for higher $\tilde{n}$ compositions. For materials containing methylammonium or cesium as the small cation to form the perovskite, different behaviors are likely to be obtained. The distinct crystal growth behavior of BNA and PEA-based layered phases in different stoichiometries and compositions during the spin-coating deposition and the subsequent annealing can be found in the works of others.^{363,452}

Benzylammonium-Mediated FAPbI_3 Perovskite Phase Stabilization Applying the defined low- $\tilde{n}$ compositions ($\tilde{n} = 1 - 3$), faces several challenges such as low photovoltaic efficiency,^{75,236,257,453} anisotropy of charge transport²³⁵ due to the anisotropic nature of the structure with low-conductivity spacer layers and generally hard to achieve phase purity.^{73,104,233,267} Thus, a slightly different approach features adding smaller amounts of the spacer cation, in this case BNA^+ , to a FAPbI_3 perovskite composition

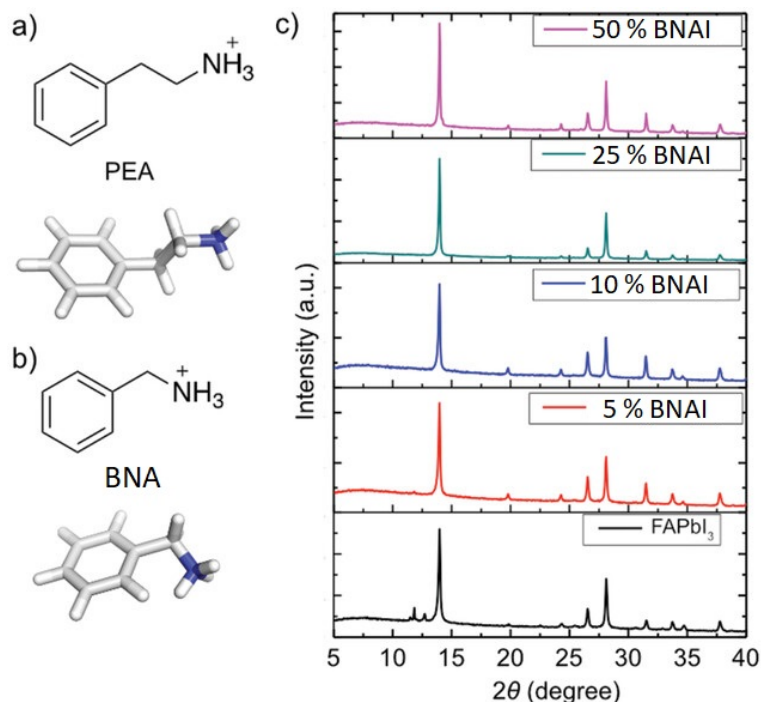
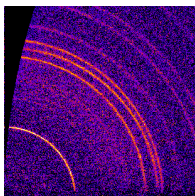
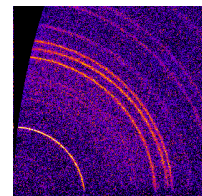


Figure 11.20: Structural representation of commonly employed (a) 2-phenylethylammonium (PEA⁺) organic spacers for 2D perovskites and (b) benzylammonium (BNA⁺) spacers employed in this study with the corresponding DFT-optimized structures (at the B3LYP 6–31G(d) level of theory). (c) X-ray diffraction patterns of the FAPbI₃(BNAI)_x perovskite films with (BNA)I percentage stated. Image taken from publication [VI].

to stabilize the α -phase. This approach is explored in publication [VI], on which this paragraph is based.

Different amounts of (BNA)I were mixed into the FAPbI₃ precursor solutions in ratios of 5 %, 10 %, 25 % and 50 % relative to the FAPbI₃ concentration. The best photovoltaic performance was observed for the thin film containing 25 % of (BNA)I, therefore this composition was chosen as the composition of interest. Details on the sample fabrication can be found in publication [VI].

The X-ray diffraction (XRD) patterns in Figure 11.20 (c) show no distinct low- q peaks which would indicate layered phases. Thus, if layered phases are present at all, they are expected to be disordered, exhibit low crystallinity or are present as multiple n phases in low concentrations. Taking a close look at the reciprocal space map of the 25 % (BNA)I thin film (Figure 11.16 (d)) reveals a faint signal of the $n = 2$ layered phase, which additionally to its low intensity shows an azimuthally distributed intensity, suggesting low orientational order and concentration. However, a remarkable absence of PbI₂ and



CHAPTER 11. LAYERED STRUCTURES

δ -FAPbI₃ can be observed in the XRD data by the disappearance of their attributed diffraction signals around $2\theta = 12-13^\circ$, suggesting a beneficial effect of the (BNA)I presence.

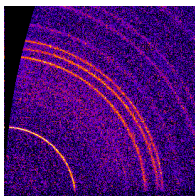
However, in the as-deposited BNA and FA-containing thin films with 25 % (BNA)I (Figure 11.18 (d)), as well as in those with $\tilde{n} = 2, 3$ compositions, the FAPbI₃ adopts the δ -phase. This implies that annealing is still necessary to convert the FAPbI₃ into the perovskite phase, which is found to be stabilized against back-conversion or degradation by (BNA)I presence.

Similarly, in the PEA-containing samples with $\tilde{n} = 2, 3$ and 25 % PEAI (Figure 11.18 (d)), FAPbI₃ adopts the δ -phase, which is another indication for a similar interaction mechanism of the PEA⁺ spacers and the perovskite layers as compared to the BNA⁺ cations. Publication [VI] further investigates the BNA⁺ interaction mechanisms with the perovskite material and the effect of mixing BNA⁺ into FAPbI₃ on its optical properties and the photovoltaic performance. As mentioned above, the photovoltaic performance as well as the shelf-life and operating stability increase with the (BNA)I ratio from 5 % (BNA)I to 25 % (BNA)I and decline again with higher ratio. For details see publication [VI] and Figure D.36 in the appendix. This is ascribed to the increased proportion of photoactive α -FAPbI₃ phase in the presence of (BNA)I.

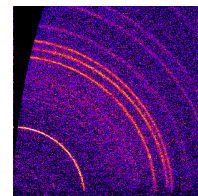
Optical analysis (Figure D.37, appendix) reveals that the optical properties of the 3D perovskite material are retained even with high (BNA)I concentrations and no indication of a layered (BNA)₂PbI₄ phase is found, which is consistent with the results from diffraction data.

Indications for close interactions of (BNA)I and the perovskite material were found by NMR, details of which are explained in publication [VI]. An alteration of the FA⁺ environment and disturbance of the symmetry of the octahedral cavities is observed as well, indicative for the formation of mixed BNA/FA-based phases, which likely are layered phases with different values of n , consistent with the faint signatures of higher n phases in the reciprocal space maps.

Therefore, even though BNA⁺ addition to the FAPbI₃ precursor solution in lower concentration does not result in a clear formation of layered phases, a potentially disordered mixture of layered higher n phases are expected to be present in small concentrations. These potentially exert a structure directing role to template α -FAPbI₃ and alter the energy landscape for the conversion to the δ -phase and therefore stabilize the α -FAPbI₃ against degradation or back transition to the photoinactive δ -phase.⁴⁵⁴



Conclusions It has been shown that both PEA⁺ and BNA⁺ spacers are capable of forming $n = 1$ and $n = 2$ layered lead iodide perovskite phases, employing FA⁺ as the central cation. Formation of the $n = 2$ phase is found to be favored in BNA-based compositions, while PEA⁺ tends to form the $n = 1$ phase as well, which exhibits generally a high degree of order and a double stacking of unit cells. Adding (BNA)I to FAPbI₃ precursor solution in substoichiometric amounts for layered phase formation is beneficial to the material phase purity, stability and photovoltaic performance, which is most likely correlated to an increased ratio of the photoactive FAPbI₃ α -phase. For this beneficial effect, layered phases are not required to be formed in considerable amounts, but small amounts of potentially different kinds of layered phase are enough to alter the energetic landscape in favor of the α -phase.



11.5 Supramolecular π -Templating in Ruddlesden-Popper Phases with Mixed Spacer Cations

So far, the previous sections discuss layered perovskite structures which include one or more small cations, but only a single type of spacer cation. Mixing of spacer cations could be another possibility to tune material properties and exploit the interactions of dissimilar molecular spacers to create new emergent properties.

In this section, binary mixtures of spacer cations are explored, specifically molecular cations bearing an aromatic moiety with and without fluorination. Phenylethylammonium (PEA^+) and benzylammonium (BNA^+) spacers were mixed with their respective fluorinated counterparts, (perfluorophenyl)ethylammonium (FEA^+) and (perfluorobenzyl)ammonium (FBNA^+). The $\text{PEA}^+/\text{FEA}^+$ results are based on publication [VII].

Applying aromatic spacers inside the organic layer could potentially exploit molecular arrangements guided by π -based interactions.^{455,456} In general, three different types of $\pi - \pi$ interaction modes can occur for aromatic compounds, which are stabilized by the molecular quadrupole moment⁴⁵⁷ and are schematically depicted in Figure 11.21. One

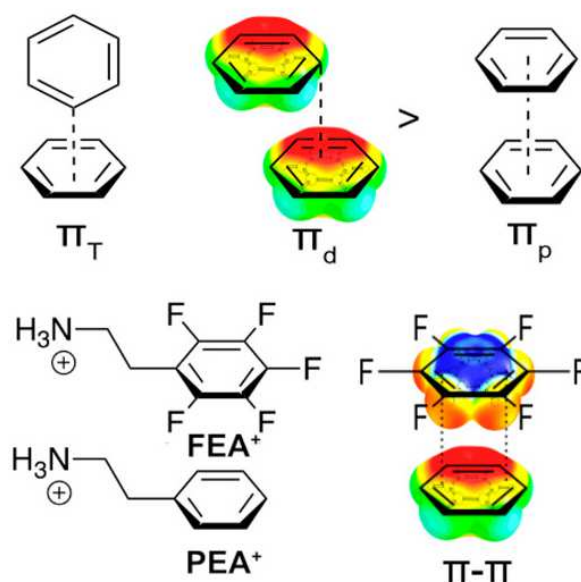
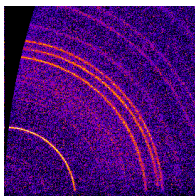


Figure 11.21: Top: Overview of possible $\pi - \pi$ interaction modes between two arenes with comparable electron-density surfaces, with different interaction strengths ($\pi_T \approx \pi_d > \pi_p$). Bottom: Arene-fluoroarene $\pi - \pi$ interaction (π_p) and the spacer cations used in this study: PEA^+ and FEA^+ . The π_p and π_d interactions of model systems are illustrated by the corresponding electrostatic potential maps. Image taken from publication [VII].



is a T-shaped alignment with an edge to face interaction of the constituting molecules, labeled as π_T in Figure 11.21. This type of alignment can be found in the herringbone structures observed in many organic semiconductors.^{457,458} For a parallel alignment of the aromatic planes, different modes can be distinguished: a parallel displaced stacking, labeled as π_d , where the aromatic systems are shifted relative to each other and a perpendicular stacking, labeled as π_p , where the molecules are stacked directly on top of each other.

Mixing aromatic compounds with fluoroaromats can favor parallel π -interactions between the fluorinated and non-fluorinated species due to the reversed electron density distribution on the molecular surface of the fluorinated molecule,^{458,459} as shown in Figure 11.21. Thus, an alternating molecular stacking is expected to enable an equimolar co-crystal stabilized by the π -interactions. Such co-crystalline structures have been observed before in mixtures of organic semiconductors, for example in the pentacene/perfluoropentacene blend.⁴⁶⁰ Exploiting similar structures inside of a layered perovskite material has the potential of enabling synergistic effects of structure stabilization, templating and charge transfer in the organic spacer layer and the inorganic perovskite components.

For the investigation of $\text{PEA}^+/\text{FEA}^+$ systems, different kinds of samples were fabricated, including mechanosynthesized powders and thin films with an $\tilde{n} = 1$ composition of layered perovskite as well as 2D/3D thin films, i.e. perovskite thin films based on a $(\text{Cs}_{0.05}\text{FA}_{0.95}\text{MA}_{0.1})(\text{PbI}_3)_{1.05}$ composition with an overlayer of the spacer that is expected to form a layered perovskite structure on the film surface. Fabrication and experimental details can be found in publication [VII]. A thorough characterization involving X-ray diffraction methods in combination with NMR crystallography was executed for the $\text{PEA}^+/\text{FEA}^+$ systems to reveal the molecular arrangement. In the second part of this section, these results are compared to those of $\text{BNA}^+/\text{FBNA}^+$ systems from X-ray diffraction on 2D/3D constructions.

Nanoscale Phase Segregation in $\text{PEA}^+/\text{FEA}^+$ Systems Formation of layered perovskite structures with PEA^+ and FEA^+ spacer cations in 2D/3D architectures is indicated by distinct low- q diffraction signals below $q = 0.5 \text{ \AA}^{-1}$ in GIWAXS (Figure 11.22 (a), (b) and (f)), which match the reported PEA-based layered structure well.⁴⁸ Radial integration of reciprocal space maps allow determination of the exact peak positions and their assignment to layered $n = 1$ and $n = 2$ structures for both spacers (Figure 11.22 (f)). The obtained layer spacings (Table 11.1) are slightly larger for FEA-based structures than with PEA^+ . The spacing of the supposed $n = 2$ structure is approximately increased by the thickness of one lead halide layer compared to the $n = 1$ structure, supporting its

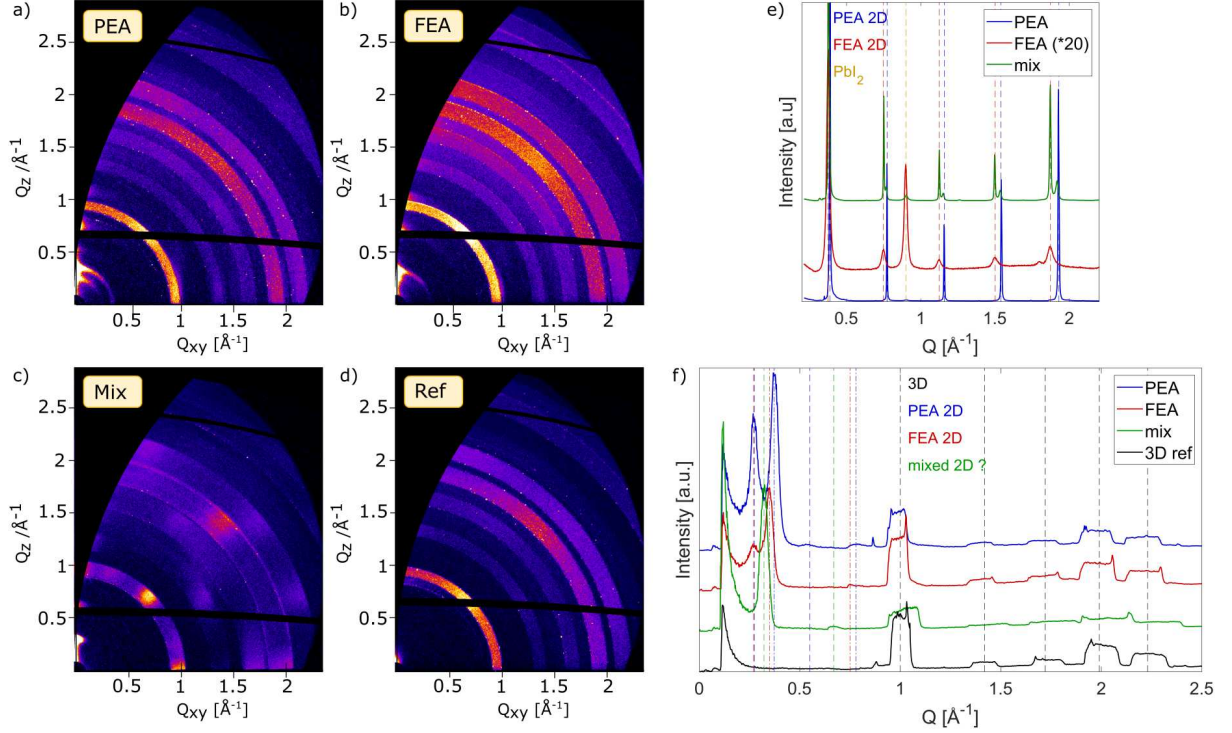


Figure 11.22: GIWAXS reciprocal space maps of 2D/3D samples with different spacer cations (a) PEA^+ , (b) FEA^+ , (c) $\text{PEA}^+ + \text{FEA}^+$ mixture, (d) 3D reference ($(\text{Cs}_{0.05}\text{FA}_{0.95}\text{MA}_{0.1})(\text{PbI}_3)_{1.05}$). (e) Powder X-ray diffraction patterns of $\tilde{n} = 1$ thin film samples with the respective compositions (data provided by Jovana Milić); (f) radial profiles of the reciprocal space maps in (a) – (d). Identified structures are marked by vertical dashed lines in (e) and (f). Parts of this figure are modified from Publication [VII].

assignment to an $n = 2$ phase. For the mixed spacer system (Figure 11.22 (c)), only one signal was observed below $q = 0.5 \text{ \AA}^{-1}$, which was located between the pure $n = 1$ and $n = 2$ phases. Its calculated layer spacing was larger than for each of the single spacer $n = 1$ structures, but still considerably smaller than an $n = 2$ structure. This indicates formation of a new mixed co-crystalline structure.

Layer spacings obtained from mechanosynthesized $\tilde{n} = 1$ powder samples are slightly smaller than those obtained from the $n = 1$ phase in the 2D/3D samples, but show a similar increase with spacer fluorination. The corresponding XRD data is found in Figure D.38 in the appendix, while calculated layer spacings are featured in Table 11.1. Interestingly, here, the mixed powder exhibits a layer spacing which is in between those of the pure spacers, indicating a mixed structure that is similar to the single spacer structures, but is consistent with a mixture of nanodomains of pure spacer structures as well.

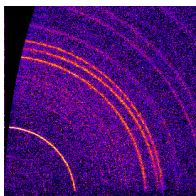


Table 11.1: Layer spacings of layered perovskite structures obtained by GIWAXS from 2D/3D structures and XRD on mechanosynthesized powders (Figure D.38, appendix). $d_{n=1}$ and $d_{n=2}$ denote layer spacings of $n = 1$ and $n = 2$ phases respectively.

	2D/3D thin film		n = 1 powder
	$d_{n=1}$	$d_{n=2}$	$d_{n=1}$
PEA ⁺	17.45 ± 0.045	24.06 ± 0.03	16.5
FEA ⁺	18.62 ± 0.07	24.19 ± 0.29	17.5
mix	20.18 ± 0.8		16.7

In the XRD patterns of the $\tilde{n} = 1$ thin film samples (Figure 11.22 (e)), however, for both pure-spacer structures the layered $n = 1$ structures were observed, while for the mixed system a phase segregation into the pure spacer-structures was apparent by the series of split peaks. This suggests that although formation of mixed-spacer structures possibly occurs in certain cases, a tendency to phase separate is discernible as well. The structure forming behavior is found to depend on the fabrication, architecture and stoichiometry of the material.

To elucidate the molecular mixing behavior, nuclear magnetic resonance (NMR) crystallography was employed (data and detailed description can be found in publication [V]). Indications for atomic scale mixing are observed by $^{19}\text{F} \rightarrow ^{13}\text{C}$ cross-polarization (CP) of the PEA^+ carbon atoms, indicating a close interaction with FEA^+ cations. However, the NMR spectra ($^1\text{H} \rightarrow ^{13}\text{C}$ CP, $^{19}\text{F} \rightarrow ^{13}\text{C}$ CP, and direct ^{19}F magic angle spinning) of the mixed spacer samples are quite similar to the pure spacer materials, indicating a nanoscale phase segregation of single-spacer domains. Thus, the local environment remains similar to the individual spacer structures but atomic level-contact is still possible due to the nanoscale domain size.

Trial structures were calculated by molecular dynamics simulations and DFT to find the closest match to explain the experimentally observed data. For the spacer layer, two different molecular alignments can occur (Figure 11.23 (a) and (b)), which feature a twisted and parallel orientation of adjacent layers. It was found that for PEA^+ , the twisted structure agrees with the experimental data, while for FEA^+ , the parallel structure is favored. Different arrangements of spacers were modeled by five different mixed models in Figure 11.23 (d), and compared to the experimental data together with a segregated model. The best fit to the experimental data was found for the segregated model, details can be found in publication [V] and the corresponding Supporting Information. To explain the

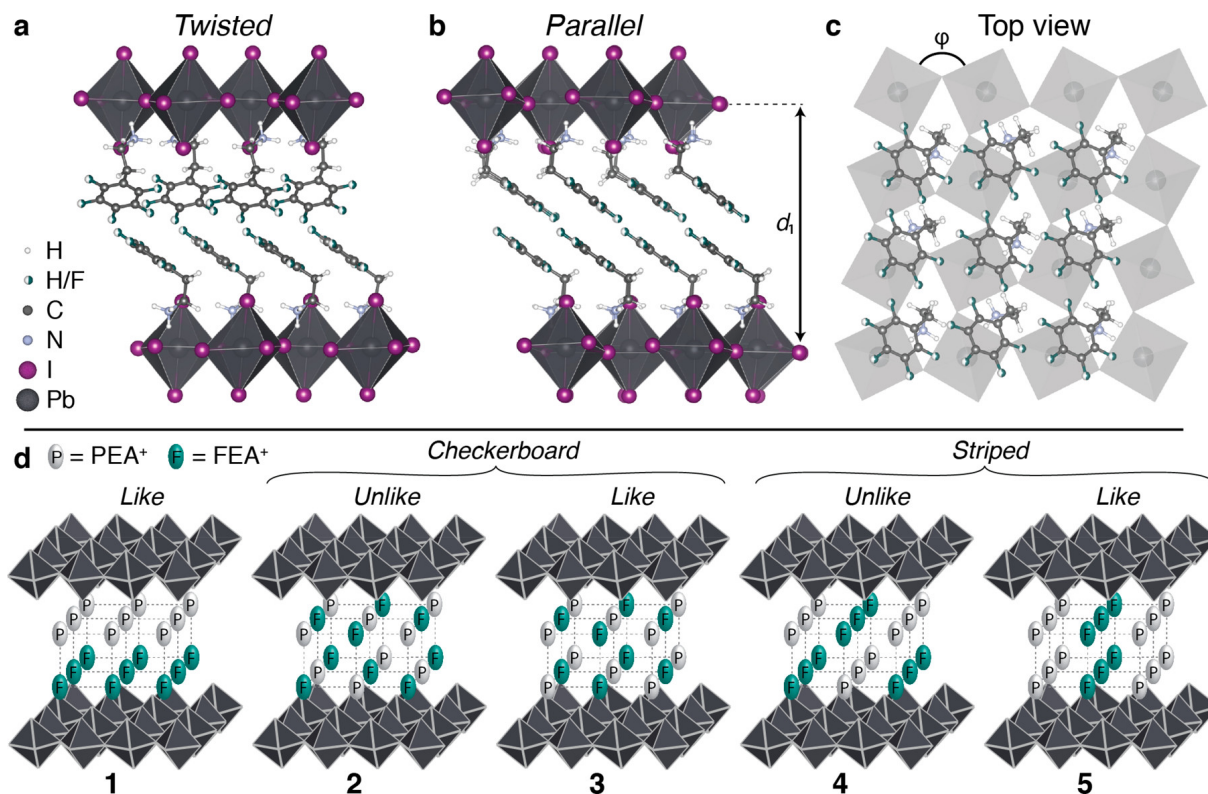
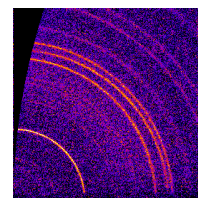
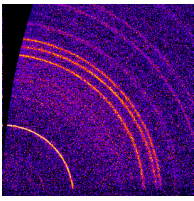


Figure 11.23: Trial structures for DFT calculations and NMR crystallography of S_2PbI_4 layered perovskites (S is PEA , FEA or a mixture of those). (a), (b) Twisted and parallel relative orientations of the aromatic rings in adjacent layers and (c) top view of the spacer layer, showing the square lattice of interstices in the inorganic layer. The interlayer spacing (d_1) and octahedral tilting (φ) are indicated as well. (d) Schematic of different possible arrangements (1–5) of PEA^+ (labeled as P) and FEA^+ (labeled as F) moieties on the two opposing lattices representing the spacer bilayer within the layered perovskite. Image modified from publication [V].

observed interactions between FEA^+ and PEA^+ and the indications of mixed structures in the X-ray data, these segregated domains are assumed to be on the nanoscale. This way it can be explained that a considerable amount of interaction still occurs and XRD showed only one average layer spacing for the mechanosynthesized powder samples, on which the NMR analysis was performed. Similar results were obtained for $\tilde{n} = 1$ thin films.

A tendency to phase segregate into single-spacer phases is likely associated with the different preferences of twisted and parallel alignments for both spacers, leading to a distinct amount of self-sorting, however limited to the nanoscale. This still allows the exploitation of potentially beneficial intermolecular interactions.

Indications of mixed structure formation are nevertheless found on the 2D/3D architec-



11.5. MIXED SPACER CATIONS

tures, as shown on the basis of GIWAXS data. A different behavior in this case might be induced by different stoichiometries or templating effects of the underlying 3D perovskite material. A clear influence of the top layer on the underlying perovskite structure can be seen as well, by comparing the azimuthal intensity distributions of the perovskite (100) signal, i.e. the ring-shaped diffraction feature around $1 \text{ \AA}^{-1}$ in Figures 11.22 (a)–(d). The sample with the mixed spacer layer exhibits a much sharper defined preferred orientation along 90° and 45° than any of the single-spacer samples and the reference. This indicates that the deposition of the mixed spacer solution on top of the perovskite thin film induces a form of orientational order in the latter, thus it is conceivable as well that in turn the presence of the bulk perovskite material influences structure formation of the layered structures and enables a new type of mixed structure.

Comparison to $\text{BNA}^+/\text{FBNA}^+$ Systems As a molecular system similar to the $\text{PEA}^+/\text{FEA}^+$ compounds, mixtures of benzylammonium (BNA^+) with its fluorinated analog, FBNA^+ were investigated in 2D/3D architectures by X-ray diffraction. The BNA^+ cation differs in only one carbon atom in the length of the anchoring chain from PEA^+

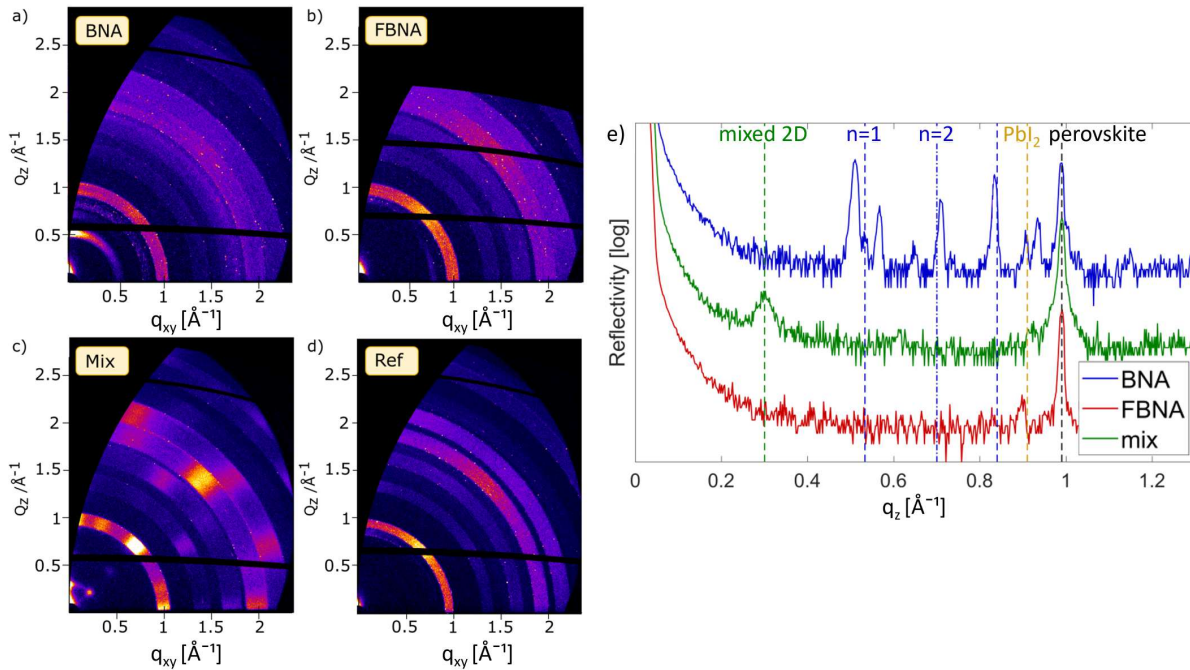
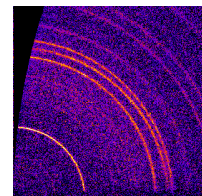


Figure 11.24: GIWAXS reciprocal space maps of 2D/3D samples with different spacer cations (a) BNA^+ , (b) FBNA^+ , (c) $\text{BNA}^+ + \text{FBNA}^+$ mixture, (d) 3D reference ($\text{Cs}_{0.05}\text{FA}_{0.95}\text{MA}_{0.1})(\text{PbI}_3)_{1.05}$ (same as Figure 11.22 (d)). (e) XRR patterns of 2D/3D samples of the respective compositions.



and thus the interactions between the aromatic cores can be expected to be similar. As in the $\text{PEA}^+/\text{FEA}^+$ system, thin films of $(\text{Cs}_{0.05}\text{FA}_{0.95}\text{MA}_{0.1})(\text{PbI}_3)_{1.05}$ perovskite material were capped with an overlayer of one or both spacers.

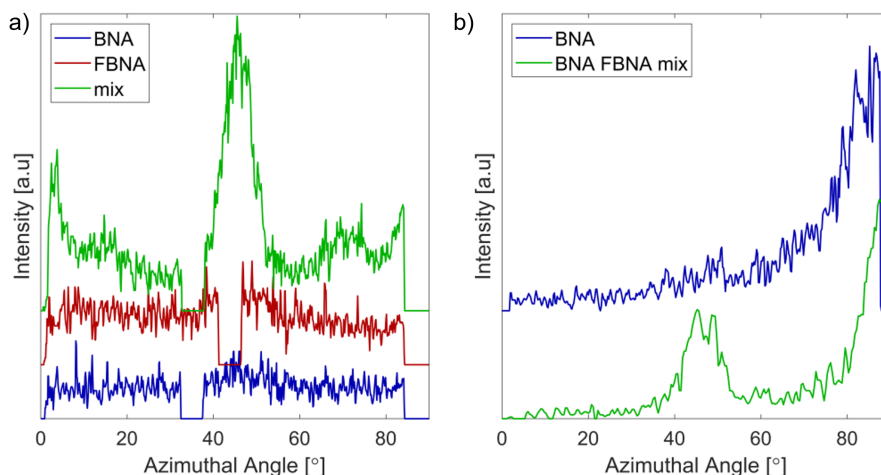
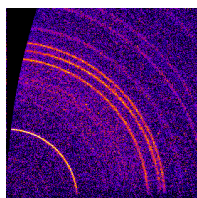


Figure 11.25: Azimuthal profiles of the (a) perovskite (110) signal, (b) layered phase signal in reciprocal space maps (see Figure 11.24) of 2D/3D samples with different spacers.

Reciprocal space maps obtained by GIWAXS (Figure 11.24 (a), (b)) as well as XRR data (Figure 11.24 (e)) indicate the formation of layered phases, represented by low- q peaks around $q = 0.5 \text{ \AA}^{-1}$, only for the BNA-based structure but not when applying FBNA^+ , where such signals are absent. With $(\text{BNA})\text{I}$ application, there were indeed several low- q signals, which indicate formation of different polymorphs of the layered structure.

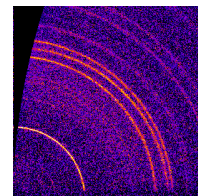
The mixed-spacer material (Figure 11.24 (c), (e)) exhibited one series of low- q peaks, which did not match any of the BNA-based layered phases and indicates the formation of a new layered phase, possibly containing both BNA^+ and FBNA^+ . This new phase exhibits a high degree of orientational order as well, visible by the sharp angular intensity maxima around 90° and 45° in the azimuthal intensity plot of the signal at $q \approx 0.3 \text{ \AA}^{-1}$ (Figure 11.25 (b)). Similar to the $\text{PEA}^+/\text{FEA}^+$ system, the orientation of the bulk perovskite material was influenced by the presence of the overlayer of layered material and a strongly preferred orientation along 90° and 45° was induced (see azimuthal profiles of the perovskite (100) signal in Figure 11.25 (a)).

This likely indicates a similar interaction in both systems with the main perovskite material, allowing the formation of mixed-spacer layered structures as well, which could be observed with GIWAXS in 2D/3D architectures of both molecular systems. The layer spacing of around $21 \text{ \AA}$ for the presumed $\text{BNA}^+/\text{FBNA}^+$ layered material is similar to the



20.18 Å observed for the presumed $\text{PEA}^+/\text{FEA}^+$ structures, suggesting a possibly similar type of mixed structure for both molecular systems.

Conclusions A combined thorough investigation of the $\text{PEA}^+/\text{FEA}^+$ mixed spacer system by X-ray diffraction and NMR crystallography helped resolve the seemingly contradictory results of mixed structure formation and phase segregation. A tendency to phase segregate into the single-spacer structures was apparent in the purely layered $\tilde{n} = 1$ structures, however it was mostly limited to the nanoscale. GIWAXS on mixed-spacer 2D/3D structures revealed indications for a different behavior in these architectures, possibly enabling the formation of new, mixed molecular structures for both $\text{PEA}^+/\text{FEA}^+$ and $\text{BNA}^+/\text{FBNA}^+$ structures. Since similar structures and effects on the bulk perovskite material could be observed for both systems, a similar interaction mechanism is assumed.

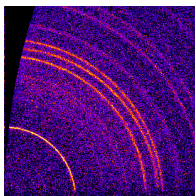


11.6 Final Remarks on the Structural Properties of Layered Perovskites

In this chapter, the structural and material properties of layered perovskite materials based on the simple aromatic spacers 1,4-phenylenedimethylammonium (PDMA^{2+}), benzylammonium (BNA^+), phenylethylammonium (PEA^+) and their derivatives were elucidated. This revealed the effects of employing spacer cations with one or two functional groups to form Dion-Jacobson or Ruddlesden-Popper types of structures, respectively, as well as using different anchor chain lengths for both types. Further compositional parameters which were explored were the halide counter ion and the stoichiometry of the precursor, i.e. the targeted layer number $\tilde{n}$ in the final thin films.

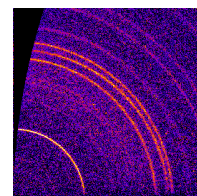
As the most distinguishable structural parameters of layered perovskite structures, the phase composition and the preferred orientation in dependence of the composition are listed in Figure 11.26. While the ability to form low dimensional phases is majorly determined by the anchoring chain length, a balanced interplay with the halide anion defines the preference for forming $n = 1$ or $n = 2$ structures. In general, $n = 1$ phases preferably form in bromide-based compositions, while $n = 2$ phase formation is likely more favored with iodide, reflecting in the majority phases formed in the respective compositions. The ratio in which $n = 1$ and $n = 2$ phases are formed in higher $\tilde{n}$ compositions is found to depend on the spacer cation as well, with BNA^+ generally featuring a higher proportion of $n = 2$ phase than PEA^+ or PDMA^{2+} , which even in higher $\tilde{n}$ compositions still exhibit considerable amounts of $n = 1$ phase. This suggests that both anchoring chain and halide enter in the phase stability, as well as the central cation for higher $\tilde{n}$ formulations, as can be seen when exchanging the formamidinium cations by cesium or methylammonium cation.⁴⁵² Thus, this statement is likely quite limited to the formamidinium-based compositions and the trends are expected to differ for different small cations. Furthermore, the shape and type of the simple aromatic spacers investigated in the presented works are a major simplification of the compositional space of layered perovskites. Differently shaped spacer cations with linear or branched aliphatic chains, as well as more bulky molecular cations or those with distinct molecular interactions between them are expected to show a different behavior.

For the present systems, while the phase formation is determined mainly by spacer cation and halide, the orientation of the resulting structures depends mainly on the stoichiometry of the precursor solution, i.e. the intended composition $\tilde{n}$ of the thin film. While $\tilde{n} = 1$ compositions tend to be generally well-oriented, utilizing higher $\tilde{n}$ compositions for thin



film deposition reduces the degree of orientation. This is especially true for iodide-based samples, while those containing bromide generally retain their orientational order better for higher $\tilde{n}$ compositions. Thus, the halide overrules the orientational order dependence on stoichiometry, making the presence of bromide the strongest factor for well-ordered structures, while these tend to be more orientationally disordered in iodide samples as soon as the composition aims at $\tilde{n} > 1$. Minor influences on the orientational order of iodide-based samples are exerted by the choice of substrate and solvent as well.

Thus, while fabrication conditions can play a role in the ordering and phase formation behavior of layered perovskite thin films, the single most effective parameter is the material composition. This is to be considered when designing materials for applications, which require a certain structural phase or degree of order.



CHAPTER 11. LAYERED STRUCTURES

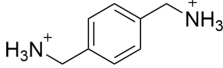
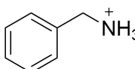
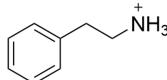
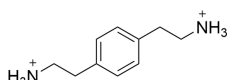
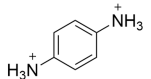
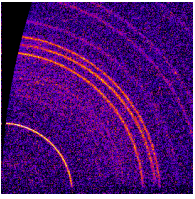
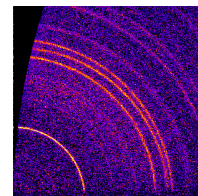
Spacer cation	Halide	Phases formed*	Orientation $\tilde{n}=1$ composition	Orientation $\tilde{n}>1$ compositions
PDMA 	I	n=1 + n=2	 + 	 + 
	Br	n=1 + n=2		 + 
BNA 	I	n=2 + n=1		 +  + 
	Br	n=1 + n=2		
PEA 	I	n=2 + n=1		
	Br	n=1 + n=2		
PDEA 	I, Br	n=1 + ?		
PDA 	I, Br	-		

Figure 11.26: Tabular representation of the main results of Chapter 11 to provide an overview over phase formation and orientational order as the two most distinguishable structural parameters. Red and green colors in the last two columns represent bromide and iodide-based structures, respectively. The lines of colored squares represent the preferred orientation of the lead halide layers, while a circle indicates random orientation. *Formation of phases in $\tilde{n} > 1$ formulations, except for PDEA^{2+} and PDA^{2+} , where only $\tilde{n} = 1$ compositions were probed. The majority phase is in large and bold script, while the minority phase is written below in smaller letters.



11.6. FINAL REMARKS

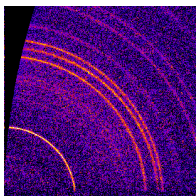


Chapter 12

Advanced Preparation Methods For Perovskite Thin Films

So far, all investigated materials are hybrid perovskite thin films deposited from variations of the wide-spread solution based processes, including one-step deposition via spin-coating, antisolvent or gas-flow-assisted deposition with subsequent thermal annealing. Although these are well-established and widely applied processes, more sophisticated methods and techniques are investigated to produce more complex architectures or improve on the drawbacks of current methods.

This chapter presents examples of such advanced preparation methods and their resulting structures, revealed by X-ray diffraction methods. In Section 12.1, spraying is introduced as an innovative method to deposit antisolvents, while Section 12.2 explores the interplay of LiBr layers and humidity in morphology modification of perovskite thin films.



12.1 Preserving the Stoichiometry of Triple-Cation Perovskites by Carrier-Gas-Free Antisolvent Spraying

Fabricating perovskite thin films with the antisolvent technique implicates several drawbacks as introduced in Section 8.2. One of its main issues is the pipetting of the antisolvent during spin-coating, which requires relatively large amounts of antisolvent to be applied in order to achieve full coverage of the spinning film.^{382, 383} However, this not only increases environmental and toxicity concerns,^{318, 461} it can be detrimental to the film quality as well. A large volume of antisolvent can, despite its low solubility for the perovskite materials and their precursors, wash away part of the material, which can lead to inhomogeneous film coverage or non-stoichiometric composition.^{382, 462} Thus, a spraying method was developed, where the antisolvent is applied from a spraying nozzle rather than a pipette, resulting in a fine mist of antisolvent covering the sample instead of one large drop. This has shown to improve the stoichiometry of the thin films as well as their performance in devices, which is reported in publication [VIII], on which the following section is based. Figure 12.1 (a), (b) schematically depicts the differences between pipetting and spraying the antisolvent onto the thin film surface during spin-coating. A triple cation composition

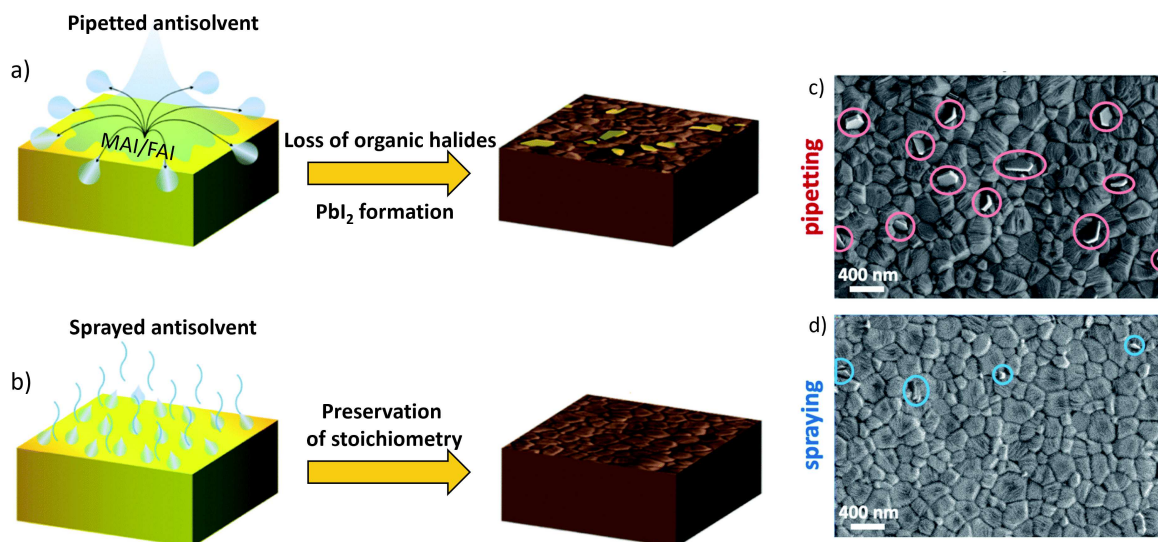
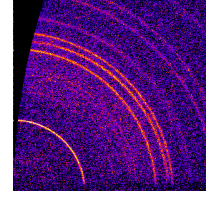


Figure 12.1: (a), (b) Schematic representation of the differences between pipetting and spraying the antisolvent and the resultant film stoichiometry. (c), (d) Scanning electron microscopy (SEM) images of triple cation perovskite $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ thin films fabricated by either (c) pipetting or (d) spraying $60\mu\text{l}$ of trifluorotoluene antisolvent. Figure modified from publication [VIII].



of stoichiometric $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ was employed for the perovskite film, while different volumes of 60, 90 and 200 μl of trifluorotoluene (TFT) antisolvent were applied via the two methods. Details on the sample preparation can be found in publication [VIII].

Via scanning electron microscopy (SEM), bright grains of inhomogeneities are found on the surface of the fabricated thin films (Figure 12.1 (c), (d)), hinting towards a segregated phase of non-stoichiometric material, possibly lead iodide.^{463, 464} These impurity crystals are significantly reduced when spraying the antisolvent rather than pipetting it.

Measuring depth-dependent GIWAXS identifies these segregated crystals on the film surface as indeed a PbI_2 phase, marked by yellow arrows in the reciprocal space maps in Figure 12.2 (a) and (b) (more in Figures D.39 and D.40, appendix). Comparing the relative signal intensities of the PbI_2 phase and the perovskite phase on the sample surface (Figure 12.2 (c)) and in the bulk (Figure 12.2 (d)), it is apparent that on the surface of the film, the PbI_2 intensity (marked by an asterisk) is increased relative to the perovskite

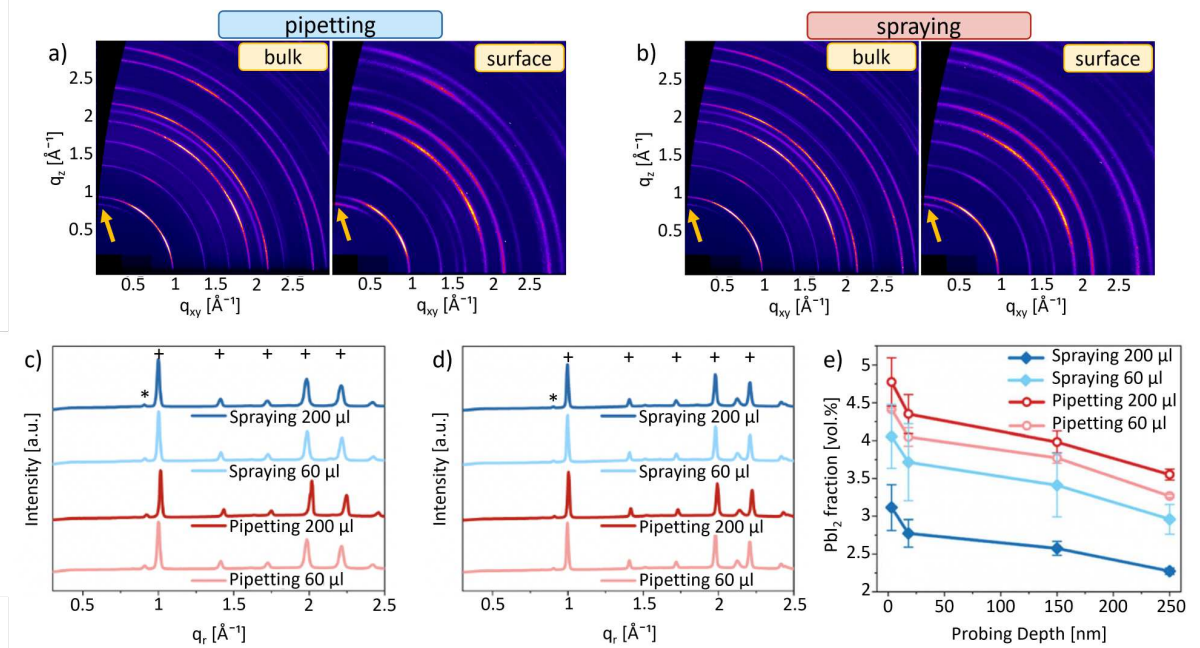
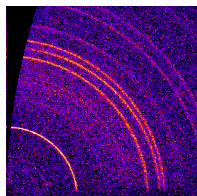


Figure 12.2: GIWAXS reciprocal space maps of triple cation perovskite thin film samples fabricated by (a) pipetting or (b) spraying 90 μl of TFT antisolvent. Incidence angles were 0.1° for surface and 0.3° for bulk analysis. (c), (d) Radial profiles of reciprocal space maps of thin films from pipetting/spraying 60 or 200 μl of TFT antisolvent at (c) the film surface (0.1° incidence angle) and (d) the bulk of the film (0.3° incidence angle). Asterisks mark the PbI_2 signal, while + marks perovskite signals. (e) Volume fraction of PbI_2 as a function of probing depth. Figure modified from publication [VIII].



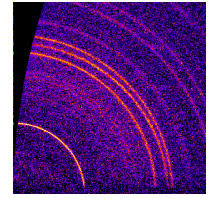
phase (marked by +) as compared to the bulk of the material. Quantitatively, this can be calculated as a volume fraction dependent on probing depth, which is varied by adjusting the GIWAXS incidence angle (Figure 12.2 (e)). Here, it is observed that the PbI_2 volume fraction is distinctly higher at the sample surface.

A clear difference between the antisolvent application techniques and volumes can be observed. Generally, the pipetted samples exhibit a higher PbI_2 fraction than their sprayed counterparts. This is in line with the observation of much more impurity crystallites on the film surface of pipetted films by SEM, identifying those as PbI_2 crystallites. However, the volume of applied antisolvent shows opposite effects for the two methods. For pipetting, more antisolvent leads to more PbI_2 , likely due to washing off more of the organic halides the more antisolvent is applied. For spraying, more antisolvent volume leads to less PbI_2 , which is expected to correlate with a better coverage of antisolvent on the sample.

This reduction in PbI_2 phase on the surface of the films fabricated by antisolvent spraying is accompanied by distinct improvements in solar cell performance, which are characterized in detail in publication [VIII].

Apart from the clear reduction in excess PbI_2 phase, no significant alterations to the perovskite structure are observed in the GIWAXS data. All samples feature a triple-cation perovskite structure, and the orientation is unchanged, featuring two azimuthal intensity maxima, indicating preferred orientation (Figure D.41 (c), appendix).

Conclusions It was shown how spraying the antisolvent when creating perovskite thin films instead of the frequently applied pipetting can preserve the stoichiometry of the fabricated thin films and reduce lead iodide impurities on the film surface. These could be identified by depth-dependent GIWAXS analysis, which helped to quantify the reduction effects. Apart from the PbI_2 reduction, no further structural changes were observed, linking the reduced amount of PbI_2 to an improved solar cell performance.



12.2 Enhancing Luminescence Efficiency by Controlled Island Formation of CsPbBr_3 Perovskite

The following section, based on publication [IX], introduces a method for forming separate perovskite islands instead of closed thin films. Such island-like structures are beneficial for light-emitting applications since the emission intensity is enhanced in these types of structures as compared to closed films or bulk materials.^{49,465} The process of island formation was observed in real time by in-situ GIWAXS and ambient humidity was identified as the key factor to drive island formation.

CsPbBr_3 was used as an active material, which was deposited by vacuum evaporation, while thin layers of LiBr (2 nm) were deposited below and on top of the perovskite thin film to modify the surface energy such that material migration into clusters occurs at room temperature.⁴⁶⁵ Additional layers of 5 nm of 1,3,5-tris(2-N-phenylbenzimidazolyl) benzene (TPBi) are deposited below and above the structure to avoid influences of the substrate. The architecture of the resulting heterostructure is shown in Figure 12.3 (a), while experimental details are published in publication [IX].

Upon removal of the thin films from the deposition chamber and exposition to ambient air, their structure is significantly altered. Already by eye, the shiny samples can be observed turning milky and dull, indicating an increased surface roughness. Indeed, by scanning electron microscopy (SEM), large micrometer sized islands are observed (Figure 12.3 (b)), which appear to be isolated from each other on the substrate surface. This island formation is accompanied by an increase in photoluminescence quantum yield (PLQY)

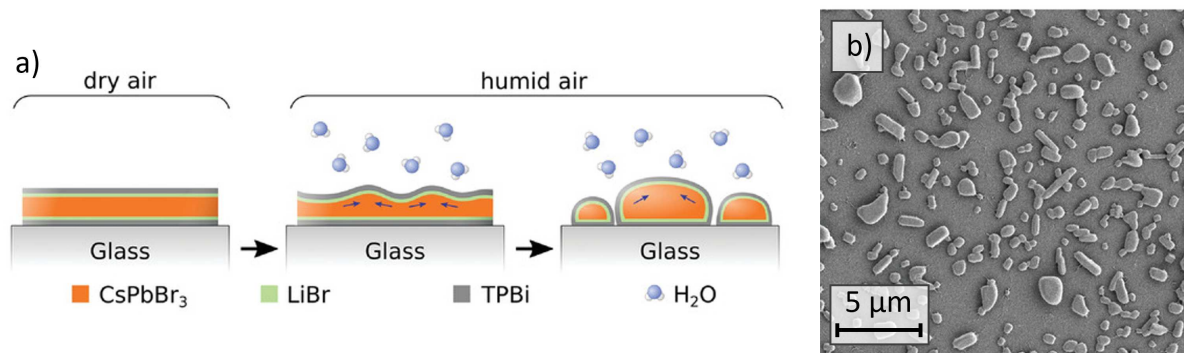
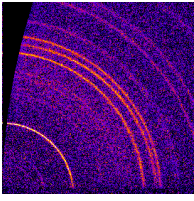


Figure 12.3: (a) Sketch of the sample architecture and the island formation upon humidity exposure. (b) Scanning electron microscope (SEM) top-view image of differently shaped islands with sizes varying from 0.6 to 2.2 μm . Image modified from publication [IX].



12.2. ISLAND FORMATION

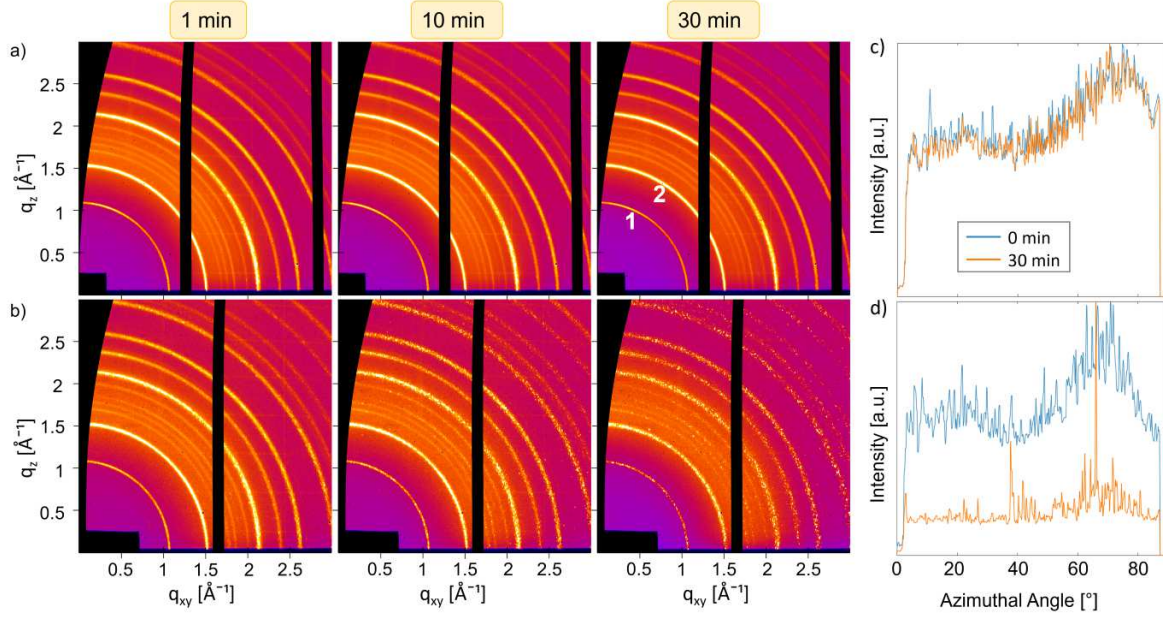
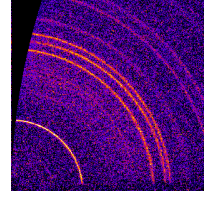


Figure 12.4: GIWAXS reciprocal space maps of CsPbBr_3 thin films after different exposure times to (a) dry air and (b) humid air. Azimuthal intensities of the (101) perovskite signal from thin films exposed to (c) dry air and (d) humid air before and after 30 min. The corresponding (101) diffraction signal is marked by 1 in (a), while (2) marks the (200) signal of $\gamma\text{-CsPbBr}_3$. Image modified from publication [IX].

by a factor of about 350 (details can be found in publication [IX]). This is ascribed to the spatial confinement of excitons, suppressing the rapid dissociation known for bulk CsPbBr_3 ,⁴⁶⁶ thus increasing the radiative recombination and the PLQY.⁴⁶⁵ In addition, the high surface roughness of island-like structures increases the out-coupling efficiency due to scattering and suppressed total internal reflection⁴⁶⁷ as compared to smooth layers.

For further insights on the island formation process upon ambient air exposure, it was monitored by in-situ GIWAXS. Initially, all samples exhibited a diffraction pattern consisting of smooth ring shaped features, indicating small and uniform crystallite sizes (Figure 12.4 (a), (b)). GIWAXS measurements were performed continuously for up to one hour of exposure to dry air or humidified air. The samples exposed to dry air do not exhibit significant alterations in their diffraction pattern for the whole time of exposure, indicating no significant change in the microstructure of the thin films. Only when the air is humidified, the diffraction pattern visibly changes after a few minutes (Figure 12.4 (b)). The smooth rings develop a grainy structure, which is an indication for enlarged crystallites since each of the grainy speckles in the diffraction ring corresponds to one



single crystalline grain. Those are observed to reduce in number, but consequently grow larger during humid air exposure. Thus, humidity is identified as the critical factor driving island formation, which is monitored taking place over the course of minutes once the samples are exposed to humid air. Due to little to no grain boundaries observed in the islands investigated by SEM, it is assumed that the islands consist of only one crystalline domain, thus the observed increase in coherently scattering domain size represents the process of island formation.

The overall preferred crystallite orientation does not change during the island growth, as indicated by a similar distribution of azimuthal intensities along the smooth and grainy perovskite diffraction rings (Figure 12.4 (c), (d)). However, a distinct difference is ob-

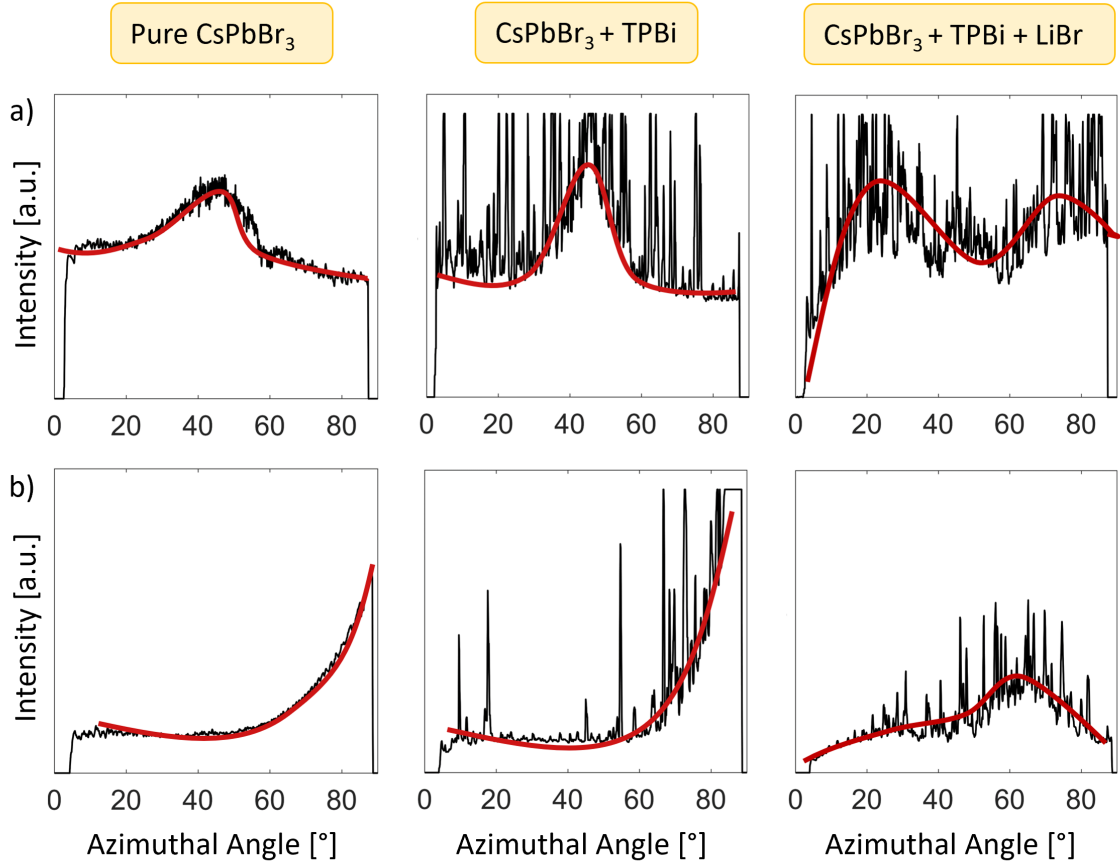
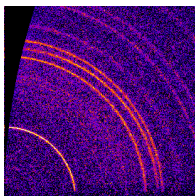


Figure 12.5: Azimuthal intensities of the perovskite signals marked by (a) 1 and (b) 2 in Figure 12.4 (a) from CsPbBr_3 -based thin films with different architectures without air or humidity exposure, showing the altered crystal orientation induced by the LiBr presence. The red lines serve as a guide to the eye. Image modified from publication [IX].

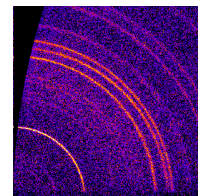


served between thin film architectures containing LiBr and those without. The direction of preferred orientation is modified once LiBr is added to the sample as compared to CsPbBr_3 thin films on glass substrates without additional layers or with only TPBi (see angular intensity profiles in Figure 12.5). Therein, the main crystal orientation is vertically aligned with the substrate, while the presence of LiBr modified it into a tilted orientation. This could be an effect of the modified surface energy upon LiBr addition, altering the preferred growth direction of the crystallites as well.

Conclusions The key role of humidity in the island formation of CsPbBr_3 induced by LiBr was revealed by in-situ GIWAXS. Island formation can be directly monitored by SEM as well, and combining both methods suggests that the islands potentially consist of single-crystalline grains. This island-like structure increases the PLQY drastically by suppressing exciton dissociation via spatial confinement. LiBr layers on the top and bottom of the films are necessary to induce island growth upon humidity exposure due to a modification in surface energy, which likewise reflects in a modification of crystallite orientation already before island formation, being retained during the growth of the islands.

12.3 Final Remarks on Advanced Preparation Methods

By these two short examples, it could be demonstrated how advanced and innovative preparation techniques can be utilized to modify the structure of perovskite thin films. The combination of X-ray scattering and further techniques is effective to elucidate the impact of the preparation method on various structural parameters such as phase composition, grain size and orientation. Thus, these parameters could not only be recorded with spatial resolution to investigate depth dependence, but temporal evolution was monitored by real-time GIWAXS as well.



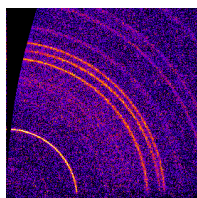
Chapter 13

Devices: Perovskite-Organic Tandem Solar Cells with Indium Oxide Interconnect

In all preceding chapters, structural studies on various perovskite architectures are presented. Mostly, though, they are bare perovskite thin films deposited on conductive substrates. However, for the chief prospective application of hybrid perovskites, solar cells, more complex architectures are required, as indicated in Section 4.3. Thus, investigation of full devices can provide more insights into the structures and their modifications in operating devices. This provides valuable information for improving device performance and stability.

The following section is based on publication [X], which reports on perovskite-organic tandem solar cells. Due to thorough optimization of all components, especially the interconnect layers, those have at the time of reporting been the most efficient monolithic perovskite-organic solar cells that have been reported. A short overview of the findings is provided, more details can be found in the publication, as well as device fabrication and characterization information.

Multijunction solar cells are able to overcome the fundamental limits of single junction cells, mainly due to reduced thermalization losses. The tunable band gaps of perovskites render them suitable for efficient tandem combinations with silicon, copper-indium-gallium-selenide (CIGS), organic semiconductors or a second perovskite cell for perovskite-perovskite tandems.^{26, 27, 468–471} Since low band gap perovskite subcells often require a composition where lead has been partially replaced by tin,^{472, 473} their stability may be fundamentally compromised, due to the oxidation tendency of tin.⁴⁶⁹ Silicon and other



commonly used solar cell materials require high temperature and high energy fabrication processes, which would hamper the vision of reducing the energy expenditure in solar cell production by employing low-temperature solution-processable ultra-thin perovskite materials. Similar processing methods and conditions of hybrid perovskite materials and organic semiconductors render those two promising partners for tandem cells.

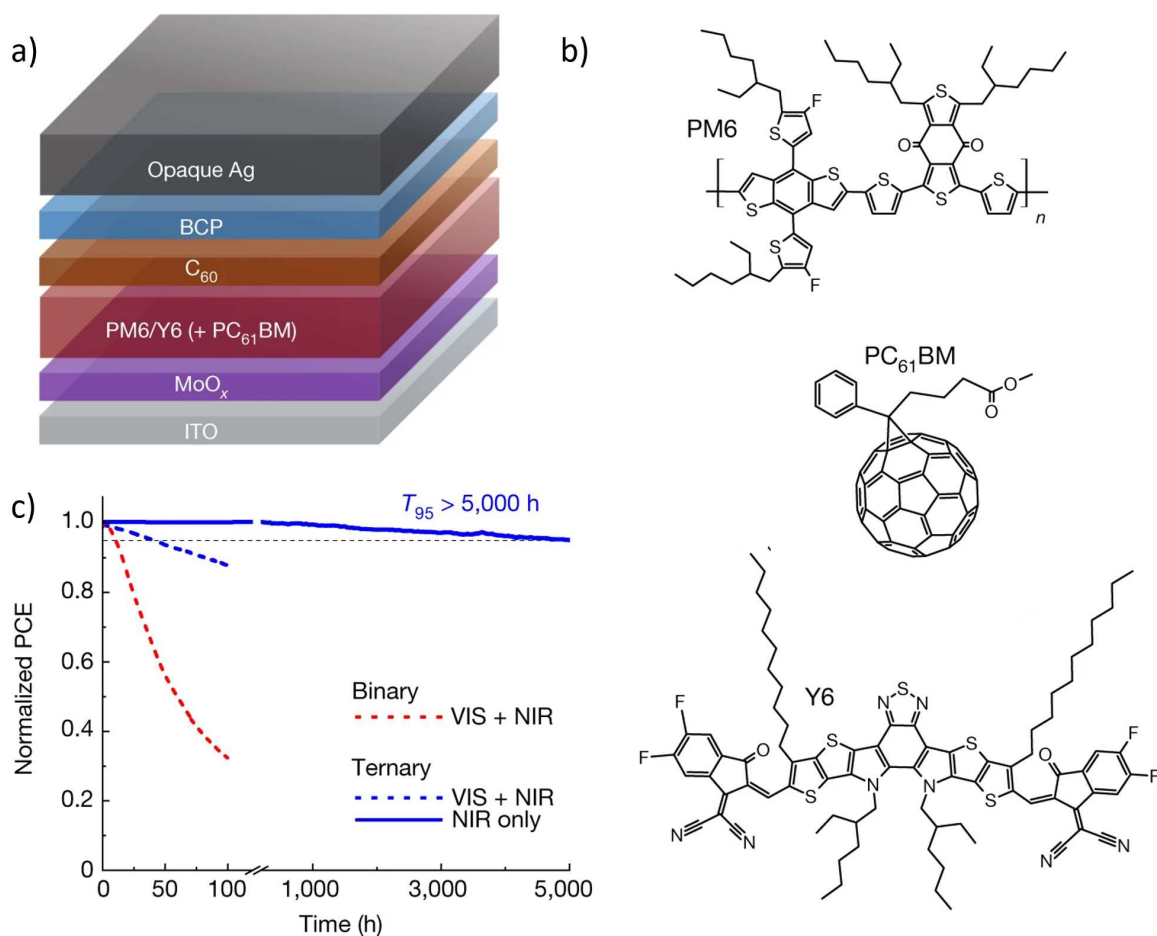


Figure 13.1: (a) Layer sequence of the single-junction organic solar cell. BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; C₆₀ = fullerene-60; ITO = indium tin oxide. (b) Structures of the molecules used in the photoactive layer (red layer in subfigure (a)). (c) Normalized power conversion efficiency (PCE) showing the long-term stability of binary and ternary organic cells continuously operated using LED light sources with emission spectra in the visible (VIS) and/or near infrared region (NIR, one-sun-equivalent, nitrogen atmosphere, 25 °C, spectra shown in publication [X]) with exciton generation on both acceptor and donor (VIS + NIR) or only on the acceptor (NIR). Note the break in the x-axis. T₉₅ denotes the time after which the PCE has dropped to 95 % of its initial value. Image modified from publication [X].

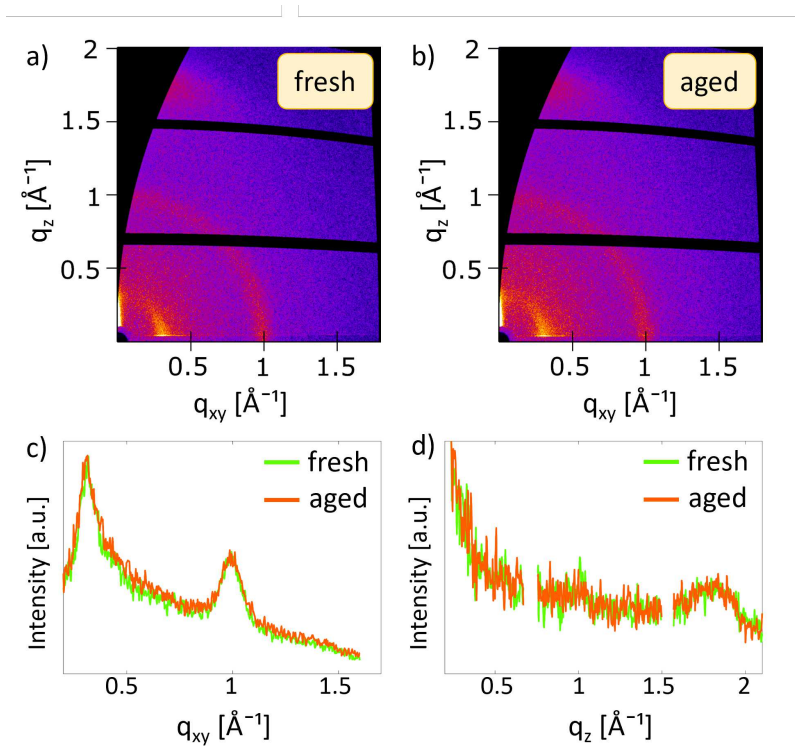
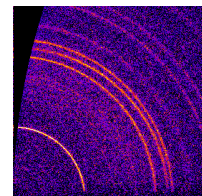


Figure 13.2: GIWAXS reciprocal space maps of (a) fresh and (b) aged (100 h LED_{VIS} + LED_{NIR}) ternary (PM6:Y6:PC₆₁BM) bulk heterojunctions. (c) horizontal and (d) vertical profiles of the reciprocal space maps showing no detectable sign for alterations in the local molecular order after aging. Image modified from publication [X].

Narrow Band Gap Organic Subcell For the narrow band gap subcell, a ternary blend of organic semiconductors was applied, containing the photoactive polymer PM6, the non-fullerene acceptor Y6⁴⁷⁵ and a small amount of PC₆₁BM, which distinctly improved the thin film morphology, stability, charge transport and extraction.^{476, 477} The molecular structures of the constituents, as well as the architecture of the organic sub-cell are shown in Figure 13.1 (a) and (b). This blend is reported to exhibit a band gap of 1.33 eV⁴⁷⁵ and shows exceptional operational and structural stability under exposure to infrared light, allowing it to retain 95 % of the original efficiency for over 5000 hours of continuous operation (Figure 13.1 (c)). Illumination with both infrared and visible light leads to an efficiency drop, which highlights the importance of employing the material as a tandem back cell, with the high energy part of the light being filtered out by the wide-band gap front-cell.

Upon prolonged exposure to visible LED light comparable to AM 1.5 G sunlight illumination, no change of the molecular packing could be observed by GIWAXS analysis (Figure

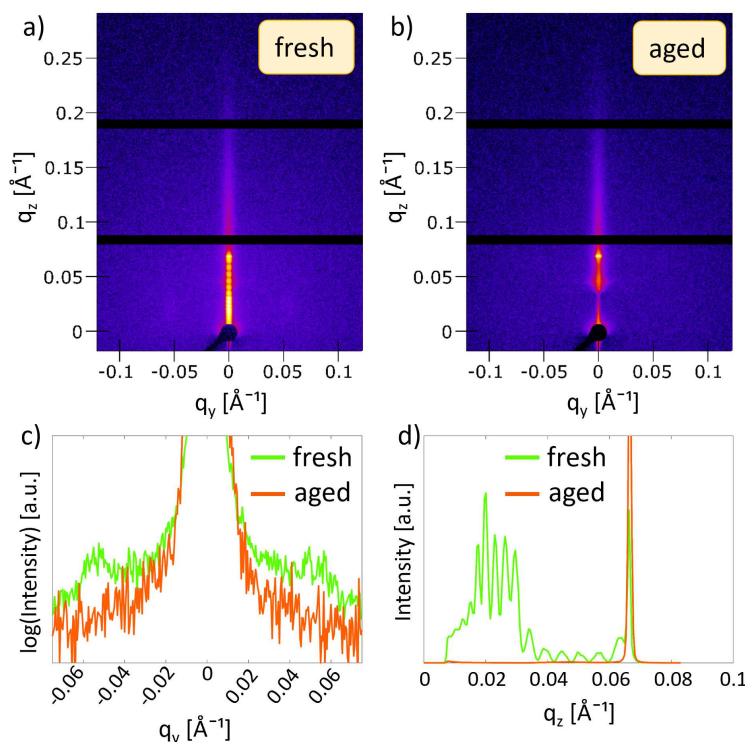
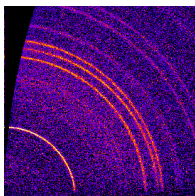
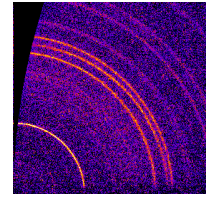


Figure 13.3: GISAXS data of (a) fresh and (b) aged ternary (PM6:Y6:PC₆₁BM) bulk heterojunctions deposited on a silicon substrate. The strong peak at around $q_z = 0.07 \text{ \AA}^{-1}$ corresponds to the reflection of the primary beam from the surface. A further signal, positioned at $q_z = 0.045 \text{ \AA}^{-1}$ for both samples corresponds to the total reflection edge of the silicon substrate (Yoneda wing⁴⁷⁴). (c) horizontal and (d) vertical profiles of the data in (a) and (b). Curves in (c) are shifted in y-direction for visibility. Image modified from publication [X].

13.2), which would indicate molecular degradation. GISAXS measurements of the same samples, investigating the surface domain properties, revealed small differences between the fresh and illuminated samples (Figure 13.3). The disappearance of the out-of-plane oscillations along the q_z -axis as well as of the very weak in-plane signals (at $q = 0.05 \text{ \AA}^{-1}$) hints to slight alterations in the correlations of surface domains. However, a clear indication of illumination induced ordering or segregation of the bulk heterojunction could not be detected, since the local molecular structure did not exhibit detectable modifications. The structural and operational stability of the organic subcell is an important contributor to the tandem cell and is found to benefit from the tandem architecture which prevents it from being exposed to high energy light that can cause increased degradation. X-ray analysis provides insights into the structural and morphological ordering which serves as



an indicator for the conservation of structural integrity upon filtering high-energy parts of the light spectrum by the front-cell.

Wide Band Gap Perovskite Subcell Employing a semi-empirical model (Figure D.42, appendix), a band gap of 1.85 eV has been determined as promising for the wide band gap front-cell to produce a high efficiency tandem stack with the above reported organic back-cell. Thus, a perovskite absorber with a composition of $\text{FA}_{0.8}\text{Cs}_{0.2}\text{Pb}(\text{I}_{0.5}\text{Br}_{0.5})_3$ was chosen to offer the required band gap value. It has been reported that the open circuit voltage (V_{OC}) of wide-gap perovskite cells is mostly limited by recombination losses at the interfaces between the perovskite thin film and the adjacent charge extraction layers,^{185, 478} thus minimizing those is the key to a high efficiency perovskite subcell. The full architecture of the perovskite subcell is shown in Figure 13.4 (a). A hole extraction layer of

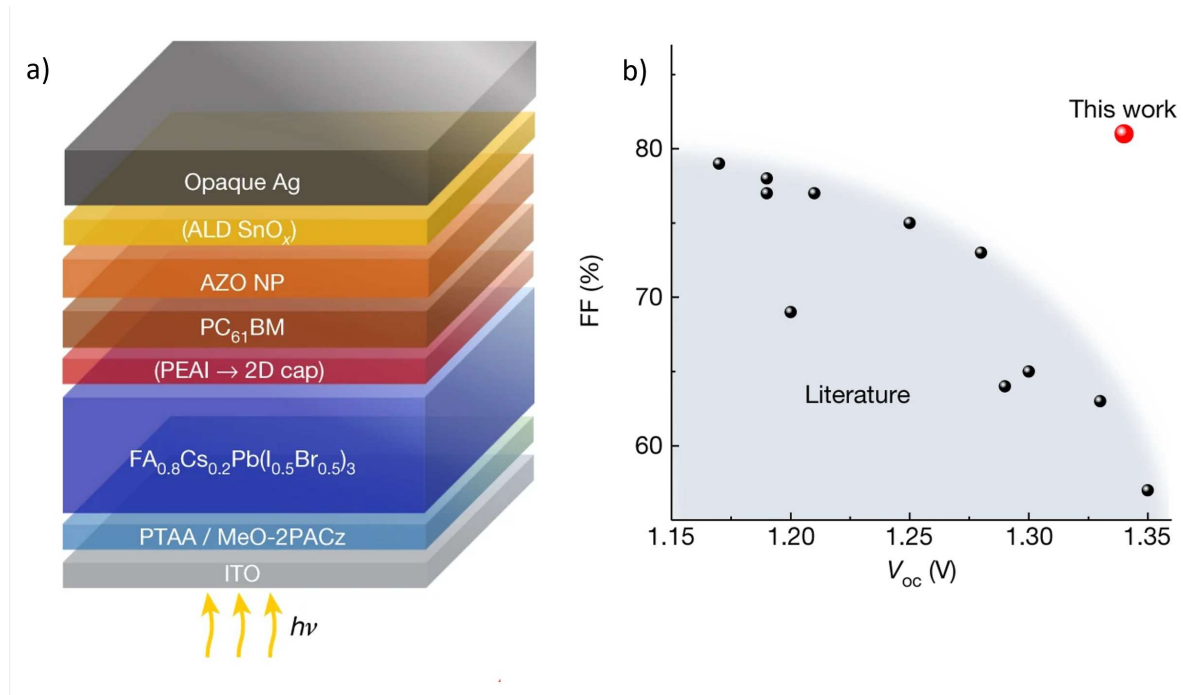


Figure 13.4: (a) Layer sequence of the *p-i-n* perovskite single junction. ALD SnO_x = tin oxide deposited by atomic layer deposition; AZO NP = aluminum zinc oxide nanoparticles; (PEA)I = phenylethylammonium iodide; PTAA = Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]; MeO-2PACz = [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid; ITO = indium tin oxide. (b) Comparison of the open circuit voltage (V_{OC}) and fill factor (FF) of the perovskite solar cells with a band gap energy $E_g = 1.85$ eV to devices (with E_g in the range of 1.8 to 1.9 eV) with high bromide content (≥ 0.4) reported in the literature. The respective references can be found in Supplementary Table 1 of publication [X]. Image adapted from publication [X].

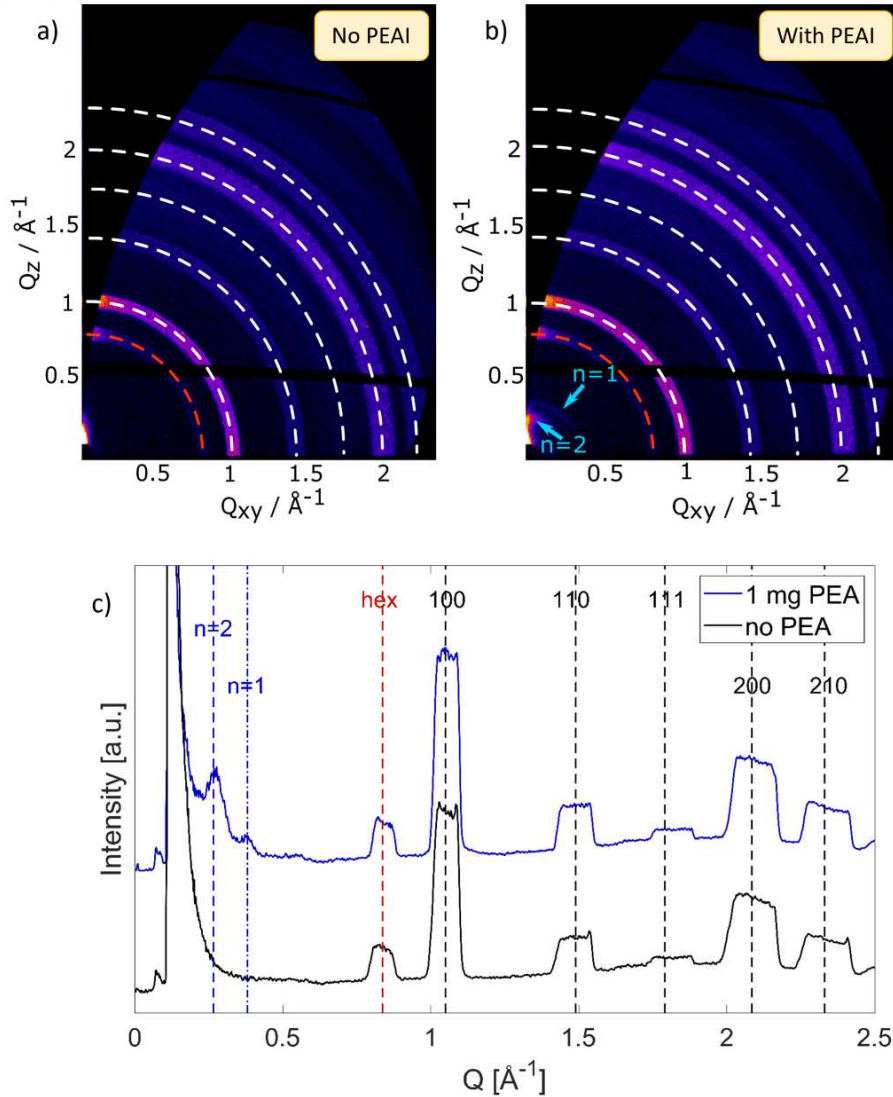
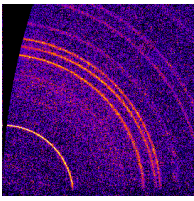
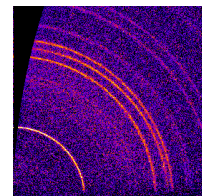


Figure 13.5: GIWAXS reciprocal space maps of $\text{FA}_{0.8}\text{Cs}_{0.2}\text{Pb}(\text{I}_{0.5}\text{Br}_{0.5})_3$ perovskite thin films (a) with and (b) without phenylethylammonium iodide (PEAI) surface treatment. (c) Radial profiles obtained by azimuthal integration of reciprocal space maps indicating the presence of (predominantly $n = 2$) layered phase in the case of the (PEA)I treated perovskite films. Vertical lines indicate $n = 1$ (blue, dot-dashed), $n = 2$ (blue, dashed) δ -FAPbI₃ (red, dashed) and perovskite α -phases (black, dashed). Numbers on the lines marking the perovskite structure indicate the corresponding Miller indices. Image modified from publication [X].

[2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz)⁴⁷⁹ is introduced, which forms a self-assembled monolayer on the indium tin oxide (ITO) bottom electrode. This enables an increased V_{OC} as compared to other commonly applied hole extraction layers by reducing interface recombination (Figure D.43 in the appendix, more details in



publication [X]). Furthermore, this self-assembled hole extraction layer is considered to mitigate halide segregation within the perovskite thin film (Figure D.44, appendix). To optimize the V_{OC} and performance of the solar cell, the second interface of the perovskite thin film, towards the electron extraction layer, is equally important. Thus, the interface between the perovskite thin film and the electron extraction layer of PC₆₁BM and Al-doped ZnO nanoparticles was equipped with a capping layer by coating the deposited perovskite thin film with phenylethylammonium iodide and subsequent annealing. Formation of a layered 2D perovskite structure on the thin film surface was indicated by GIWAXS analysis (Figure 13.5). Layered phases with $n = 1$ and $n = 2$ were identified, their peak positions are marked in the radial profiles in Figure 13.5 (c). Their presence lowers the valence band maximum on the surface of the perovskite film, thereby preventing holes from entering the electron extraction layer. This enables a selective electron extraction while maintaining low surface defect density to minimize interface recombination losses (for details see publication [X] and the corresponding Supporting Information). The mitigation of the interface losses by choosing suitable charge extraction layers and applying a 2D perovskite capping layer enables a wide band gap perovskite subcell with exceptionally high V_{OC} and fill factor (Figure 13.4 (b)), providing a record combination.

Low-Loss Indium Oxide Interconnect One key component of monolithic tandem solar cells is the interconnect between the subcells (Figure 13.6). In a p-i-n tandem, this interconnect layer facilitates the recombination of electrons from the bottom perovskite cell with the holes from the top organic cell, ideally without any loss of open circuit voltage and fill factor. Stacking the subcells directly on top of each other leads to a high Schottky barrier causing poor current-voltage (J-V) characteristics for the connecting interface.

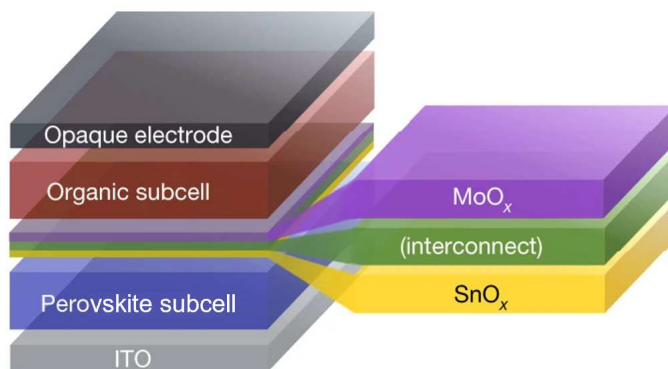


Figure 13.6: Schematic of a perovskite-organic tandem cell with indium oxide (InO_x) as interconnect. Image taken from publication [X].

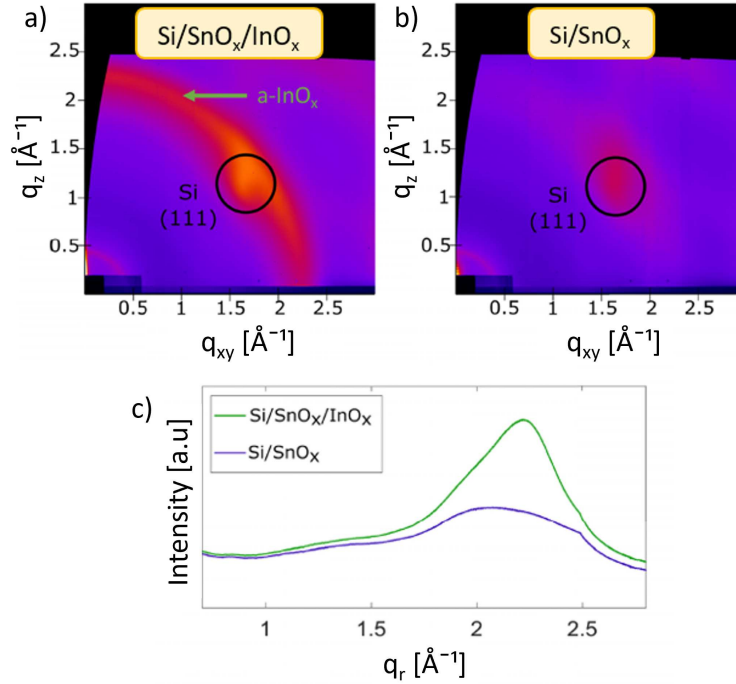
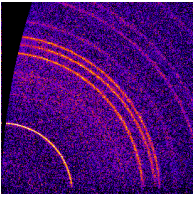
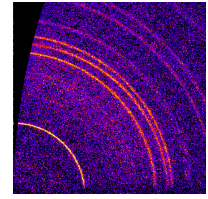


Figure 13.7: GIWAXS reciprocal space maps of (a) 20 nm InO_x on 20 nm SnO_x and (b) only 20 nm SnO_x on silicon substrates (incidence angle 0.3°, probing depth > 500 nm). The broad signal of amorphous InO_x is indicated by a green arrow. With the probing depth exceeding the thickness of the deposited layers, the (111) reflection of the silicon substrate can be seen as well (marked by a black circle). (c) Radial profiles of the reciprocal space maps in (a) and (b). Image modified from publication [X].

Inserting a very thin (1.5 nm) indium oxide layer deposited by atomic layer deposition (ALD) drastically improves the J-V behavior and enables an ohmic connection within the MoO_x/InO_x/SnO_x stack for barrier-free charge transport (Figure D.45, appendix, more details in publication [X]).

The interconnect layers are shown to be continuous with abrupt interfaces and an amorphous structure, as indicated by GIWAXS (Figure 13.7), where a broad signal indicative of amorphous indium oxide can be seen. Even though the combination of indium oxide (InO_x) and tin oxide (SnO_x) might potentially form indium tin oxide (ITO), this is not observed here. Diffraction signals of any crystalline oxides are absent in the GIWAXS data, which only feature amorphous scattering of the respective compounds.

The formation of distinct layers was confirmed by ultraviolet photoelectron spectroscopy (UPS) as described in publication [X]. Optical losses are negligible due to the low thickness of the InO_x layer.



Perovskite-Organic Tandem Solar Cells With these considerations for the subcells, the most efficient monolithic perovskite-organic tandem solar cells at the time of reporting could be realized. Details on the device characteristics can be found in Figure 13.8 and in publication [X], with the champion devices reaching a stabilized power conversion efficiency (PCE) of 24 % (certified 23.1 %). This is enabled by the high V_{OC} and fill factor of the perovskite subcell due to the optimized charge extraction layers, a high efficiency of the organic subcell in the near-IR region and its good operational stability as well as the lossless interconnection by the ultra-thin InO_x layer.

This enables stable tandem cells, whose performance stays unchanged over 1000 h in inert atmosphere and retains 80 % of the initial intensity under 130 h of continuous maximum power point (MPP) tracking (Figure 13.9). The temporal behavior of the tandem under continuous operation is essentially governed by that of the perovskite subcell.

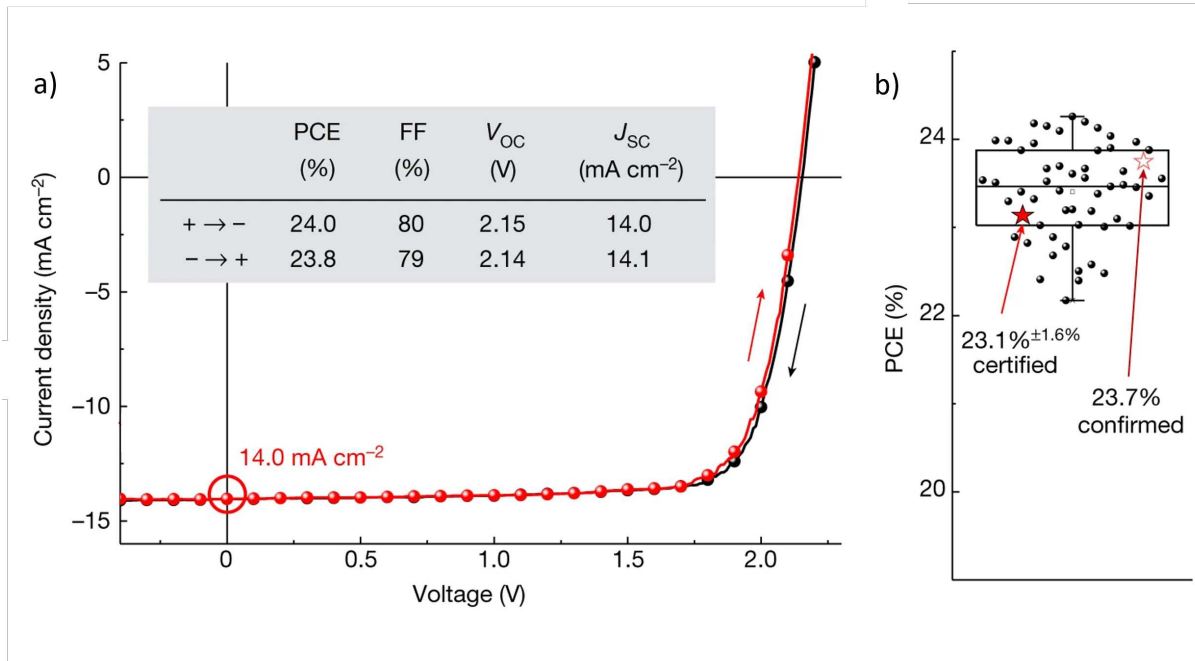


Figure 13.8: (a) Current-voltage (J - V) characteristics of a tandem cell, with derived power conversion efficiency (PCE), fill factor (FF), open-circuit voltage (V_{OC}) and short-circuit current (J_{SC}) shown in the inset. (b) Statistical data of 48 tandem solar cells as derived from reverse J - V scans, including the certified and confirmed values measured by the Fraunhofer ISE Callab. Median line with upper and lower box ranges denoting the 25 % and 75 % margins. The bars denote the outermost data points that are still inside another 1.5 interquartile range. Image modified from publication [X].

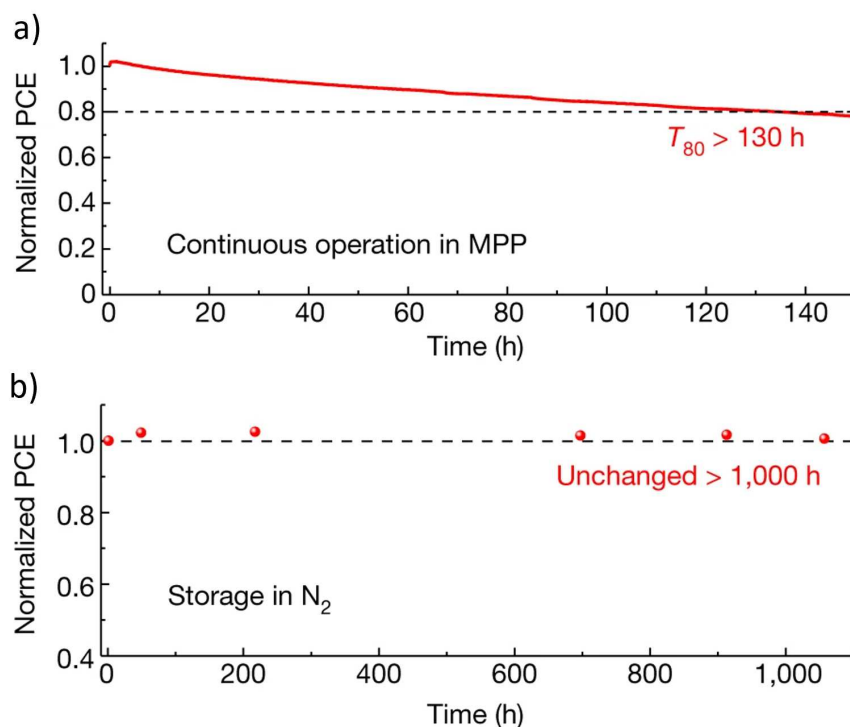
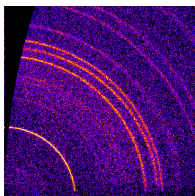
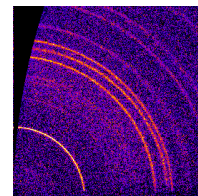


Figure 13.9: Normalized power conversion efficiency (PCE) as a measure of stability of the tandem cells under continuous operation (a) in the maximum power point and (b) when stored in nitrogen atmosphere. Image modified from publication [X].

Conclusions Fabrication of a record-breaking monolithic perovskite-organic tandem solar cell was achieved by carefully tuning the parameters of all components of the subcells. This included adjusting the band gaps of both subcells by employing an appropriate mixture of organic semiconductors for the narrow-band gap subcell and an optimized perovskite composition for the wide-band gap subcell. Adjusting the morphology of the organic thin film by employing a ternary blend and choosing appropriate charge extraction layers, including a 2D perovskite capping layer for the perovskite subcell were further major benefits. The key to unlocking superior tandem performance, however, is the interconnect layer between the subcells, which enables near lossless performance.

X-ray investigations were essential to assess critical structural parameters for the success and stability of the devices, such as modifications in the organic layer upon illumination, the amorphous nature of the interconnect and the formation of a 2D capping layer on the perovskite thin film. Thus, systematic optimization of all these parameters could be implemented to allow creation of tandem solar cells with exceptional performance.

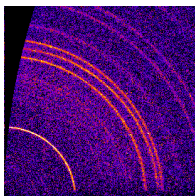
IV SUMMARY AND OUTLOOK



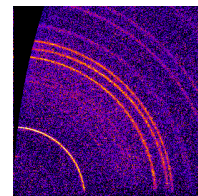
This thesis provides an overview of several studies on perovskite thin films employing X-ray diffraction methods. Information on the component mixing, additives, layered structures, sophisticated fabrication methods and functional photovoltaic devices could be obtained, showcasing the wide variability of both perovskite structures and architectures and X-ray methods as a non-destructive and time resolved tool. These results map out routes for further research.

The main findings of the presented studies, including their possibilities and open challenges are:

- Quantification of the phase composition of formamidinium lead iodide (FAPbI₃)-based perovskite thin films depending on the cation mixture is provided. Including smaller inorganic cations such as cesium and rubidium effectively stabilizes the FAPbI₃ α -phase and shows distinct effects on crystal structure and phase distribution (Section 9.1). Inclusion of the larger imidazolium cation, however, leads to an increase of δ -phase presence in FAPbI₃-based compositions (Section 9.3). Since one of the greatest assets of perovskite materials is their component miscibility, quantitative results on cation mixing can help to create stable and efficient materials by selecting appropriate mixing components and ratios.
- Confirmation of a gradient doping profile upon surface functionalization by a cesium-crown ether complex (Section 9.2) is provided. This opens new pathways for generating stable and functional FAPbI₃-based perovskite thin films by infusing the surface with dopants while retaining the optical properties of the bulk. A proof of principle is provided, opening up new synthesis pathways.
- The segregated crystallization sequences of mixed halide methylammonium-based perovskite thin films are elucidated. Halide mixing only occurs upon thermal annealing, while the reversible halide segregation process could be monitored in real time by in-situ GIWAXS as well, to reveal its gradual nature (Section 9.4). The finding of phase segregated crystallization is expected to help unravel the driving forces behind halide segregation and find new stabilization strategies to be applied already during thin film deposition to favor mixing. This crystallization behavior hints towards an intrinsic segregation tendency, while the entropic contribution by heating the material favors mixing. This knowledge enables the design of fabrication procedures for enhanced homogeneity of mixed films with increased stability against phase segregation. This implies that augmentation or modification of the energy landscape can be devised to prevent segregation.



- Pinpointing the effect of the thiourea additive during thin film growth to the thermal annealing as the critical step is achieved. Two distinct effects are observed, inducing grain growth irrespective of material composition and conversion kinetics, as well as creating preferred orientation in thin films containing methylammonium iodide (Chapter 10). Additives such as thiourea are a widespread method to manipulate perovskite thin film morphology. While the critical step as well as the composition dependence could be elucidated, open questions are still the kinds of interactions leading to the two distinct effects of grain growth and orientation, which may be caused by two different mechanisms or both be a result of modified energetics upon thiourea addition. While a general modification of (surface) energetics by thiourea is considered to be responsible for the large grains and suppression of hexagonal phase, exact values are missing. Similarly, for the crystallite orientation, which is suggested to be specific to compositions based on methylammonium iodide, the nature of possible interactions and the exact working principle of the influence on material texture is a subject for further research.
- Layered phase formation and ordering behavior in 2D perovskite materials based on aromatic spacer cations is systematically investigated, where the formation ability of 2D perovskites is determined mainly by the spacer cation, while the relative preference of $n = 1$ or $n = 2$ phases depends on the halide anion as well. The stoichiometry of the precursor solution mainly determines the orientational order of the thin film in iodide-based compositions (Sections 11.1–11.4). Since layered structure formation thus depends mainly on the material composition, especially the spacer cation and the halide, extending the general view towards more, differently shaped spacers will help elucidate general trends and stability determining factors which could be useful in designing materials. The trends provided in this work based on simple aromatic spacers with formamidinium-based compositions for higher n structures could be extended to differently shaped molecular cations and other small cations such as methylammonium or cesium to achieve a general guideline for designing stable and functional layered perovskite materials. Mixing aromatic spacer cations with their fluorinated analogs, although showing segregation tendencies in $\tilde{n} = 1$ compositions, enables formation of new mixed structures in 2D/3D architectures (Section 11.5). Since mixing spacer cations can potentially enable new emergent properties in perovskite materials, these architectures are worth exploring further to combine perovskite structures with various organic spacers that exhibit specific interactions within the organic layers, extending the variety of these structures and

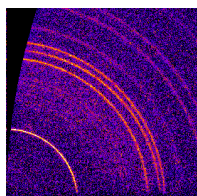


possible applications further.

- The effects of advanced preparation methods such as antisolvent spraying and controlled island formation on the crystal structure, morphology and phase composition are investigated in real time (Chapter 12). Monitoring these preparation methods and their distinct effects by X-ray diffraction can provide a valuable tool to tune the process parameters even further to optimize thin film quality. This involves the effects of surface functionalization and stabilization by assessing the phase composition and modification of structural parameters as well as real-time monitoring. These analyses are demonstrated for several different types of advanced treatments, but can be extended to more, industrially relevant processes to optimize their outcome for successful upscaling and commercialization of perovskite solar cells.
- Beside the perovskite thin film, further device components can be examined by X-ray scattering methods as well. This includes the interconnect layers and organic subcell in a perovskite-organic tandem architecture to elucidate critical structural parameters and possible degradation to improve and stabilize device performance (Chapter 13). Probing the different components proves useful to ensure structural integrity and stability of all components to provide optimum device functionality. This is crucial for applications since not only the perovskite thin film has to exhibit optimum performance and stability, but the other components have to match up as well.

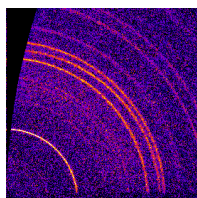
Thus, it has been shown, using X-ray scattering methods, how investigating the structural parameters starting from deposition of the precursor solution, during preparation by various methods and treatments, up to final films and devices can contribute to a large variety of open questions in perovskite research. In combination with further investigation methods and tools, X-ray scattering provides valuable answers to important questions including areas such as component mixing, additives, crystallization sequences, structure formation and device stability. Further steps for research on these topics are laid out as well as suggestions provided how to extend the current results for building a systematic approach to fabricate stable and functional perovskite thin films by making informed choices on material composition, deposition and treatment methods as well as device architectures.

This will help pave the way for perovskite-based applications in photovoltaics and further technological areas by exploiting their potential for technological utilization.

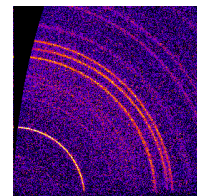


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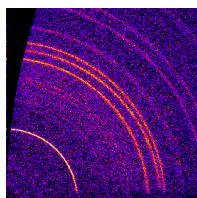
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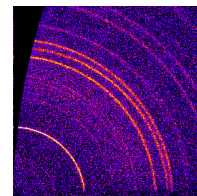
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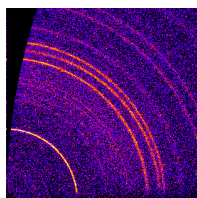
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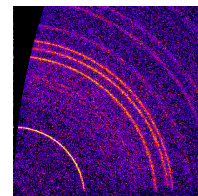
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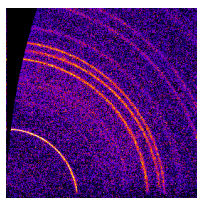
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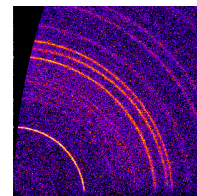
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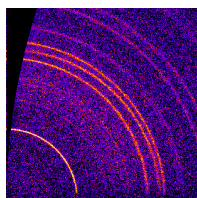
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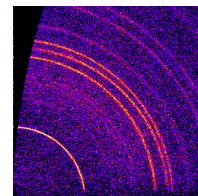
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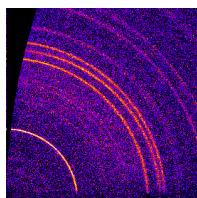
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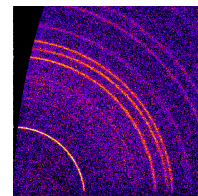
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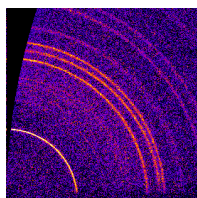
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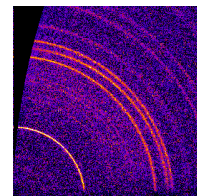
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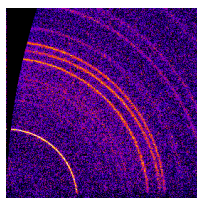
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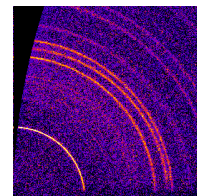
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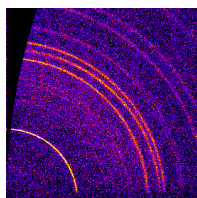
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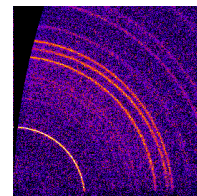
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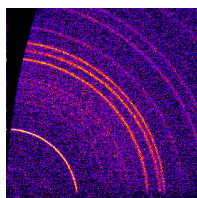
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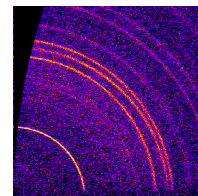
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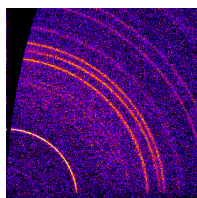
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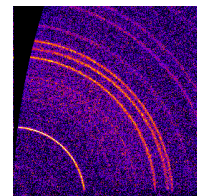
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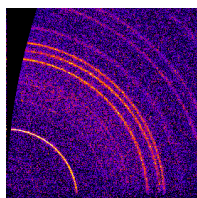
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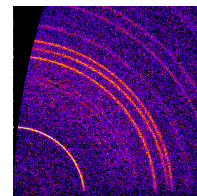
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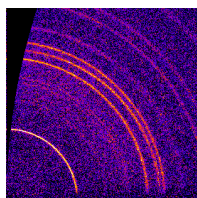
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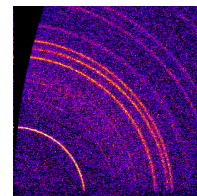
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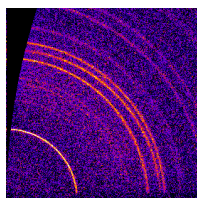
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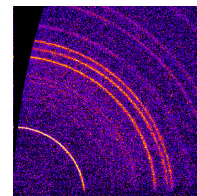
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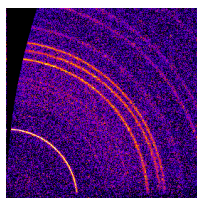
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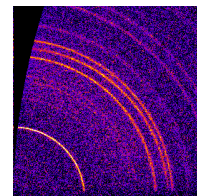
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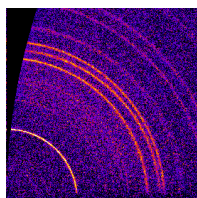
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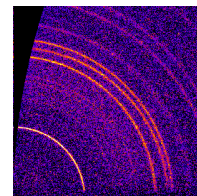
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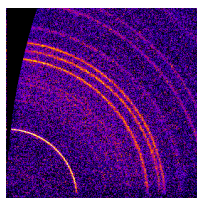
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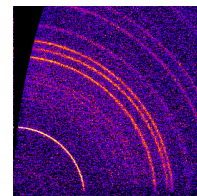


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APPENDICES



Appendix A

List of Own Publications

- I “Quantifying Stabilized Phase Purity in Formamidinium-Based Multiple-Cation Hybrid Perovskites”

L. Merten, A. Hinderhofer, T. Baumeler, N. Arora, J. Hagenlocher, S. Zakeeruddin, M. Dar, M. Grätzel, and F. Schreiber

Chem. Mater. **2021**, *33*, 2769

DOI: 10.1021/acs.chemmater.0c04185

Own contributions: X-ray data analysis and writing of the manuscript.

Contributions by collaborators: Sample fabrication, Photovoltaic, photoluminescence and X-ray measurements as stated in the publication.

- II “Multimodal Host-Guest Complexation for Efficient and Stable Perovskite Photovoltaics”

H. Zhang, F. T. Eickemeyer, Z. Zhou, M. Mladenović, F. Jahanbakhshi, L. Merten, A. Hinderhofer, M. A. Hope, O. Ouellette, A. Mishra, P. Ahlawat, D. Ren, T.-S. Su, A. Krishna, Z. Wang, Z. Dong, J. Guo, S. M. Zakeeruddin, F. Schreiber, A. Hagfeldt, L. Emsley, U. Rothlisberger, J. V. Milić, and M. Grätzel

Nat. Commun. **2021**, *12*, 3383

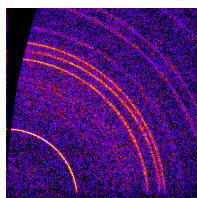
DOI: 10.1038/s41467-021-23566-2

Own Contributions: X-ray measurements and analysis

Contributions by collaborators: Sample fabrication, all further measurements, analyses and manuscript writing

- III “Halide Segregated Crystallization of Mixed Halide Perovskites Revealed by In-Situ GIWAXS”

L. Merten, T. Eberle, E. Kneschaurek, N. Scheffczyk, P. Zimmermann, A. Khadiev, F. Bertram, I. Zaluzhnyy, F. Paulus, A. Hinderhofer and F. Schreiber



ACS Appl. Mater. Interfaces **2024**, *16*, 8913

DOI: 10.1021/acsami.3c18623

Own Contributions: Conceptualization, sample preparation (in-situ samples), X-ray measurements and analysis, manuscript writing.

Contributions by collaborators: Additional sample fabrication (ex-situ samples), solution preparation, supporting X-ray measurements.

IV “Formamidinium-Based Dion-Jacobson Layered Hybrid Perovskites: Structural Complexity and Optoelectronic Properties”

M. C. Gélvez-Rueda, P. Ahlawat, L. Merten, F. Jahanbakhshi, M. Mladenović, A. Hinderhofer, M. I. Dar, Y. Li, A. Dučinskas, B. Carlsen, W. Tress, A. Ummadisingu, S. M. Zakeeruddin, F. Schreiber, A. Hagfeldt, U. Rothlisberger, F. C. Grozema, J. V. Milić, and M. Grätzel

Adv. Funct. Mater., **2020**, *30*, 2003428

DOI: 10.1002/adfm.202003428

Own Contributions: X-ray measurements and analysis, writing of manuscript paragraphs

Contributions by collaborators: Sample fabrication, all further measurements, analyses and manuscript writing

V “The Role of Alkyl Chain Length and Halide Counter Ion in Layered Dion-Jacobson Perovskites with Aromatic Spacers”

A. Dučinskas, G. Fish, M. Hope, L. Merten, D. Moia, A. Hinderhofer, L. Carbone, J-E. Moser, F. Schreiber, J. Maier, J. Milić, and M. Grätzel

J. Phys. Chem. Lett. **2021**, *12*, 10325

DOI: 10.1021/acs.jpcclett.1c02937

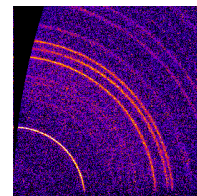
Own Contributions: X-ray measurements and analysis.

Contributions by collaborators: Sample fabrication, all further measurements, analyses and manuscript writing.

VI “Benzylammonium-Mediated Formamidinium Lead Iodide Perovskite Phase Stabilization for Photovoltaics”

A. Q. Alanazi, M. H. Almalki, A. Mishra, D. J. Kubicki, Z. Wang, L. Merten, F. T. Eickemeyer, H. Zhang, D. Ren, A. Y. Alyamani, H. Albrithen, A. Albadri, M. H. Alotaibi, A. Hinderhofer, S. M. Zakeeruddin, F. Schreiber, A. Hagfeldt, L. Emsley, J. V. Milić, and M. Grätzel

Adv. Funct. Mater. **2021**, *31*, 2101163



APPENDIX A. LIST OF OWN PUBLICATIONS

DOI: 10.1002/adfm.202101163

Own Contributions: X-ray measurements and analysis.

Contributions by collaborators: Sample fabrication, all further measurements, analyses and manuscript writing.

VII “Nanoscale Phase Segregation in Supramolecular π -Templating for Hybrid Perovskite Photovoltaics from NMR Crystallography”

M. A. Hope, T. Nakamura, P. Ahlawat, A. Mishra, M. Cordova, F. Jahanbakhshi, M. Mladenović, R. Runjhun, L. Merten, A. Hinderhofer, B. I. Carlsen, D. J. Kubicki, R. Gershoni-Poranne, T. Schneeberger, L. C. Carbone, Y. Liu, S. M. Zakeeruddin, J. Lewinski, A. Hagfeldt, F. Schreiber, U. Rothlisberger, M. Grätzel, J. V. Milić, and L. Emsley

J. Am. Chem. Soc. **2021**, *143*, 1529

DOI: 0.1021/jacs.0c11563

Own Contributions: X-ray measurements and analysis.

Contributions by collaborators: Sample fabrication, all further measurements, analyses and manuscript writing.

VIII “Preserving the Stoichiometry of Triple-Cation Perovskites by Carrier-Gas-Free Antisolvent Spraying”

O. Telschow, M. Albaladejo-Siguan, L. Merten, A. D. Taylor, K. P. Goetz, T. Schramm, O. Konovalov, M. Jankowski, A. Hinderhofer, F. Paulus, F. Schreiber, and Y. Vaynzof

J. Mater. Chem. A **2022**, *10*, 19743

DOI: 10.1039/d1ta10566c

Own Contributions: planning and supervision of X-ray measurements, data analysis.

Contributions by collaborators: Sample fabrication, all measurements, further analyses and manuscript writing.

IX “Enhancing Luminescence Efficiency by Controlled Island Formation of CsPbBr₃ Perovskite”

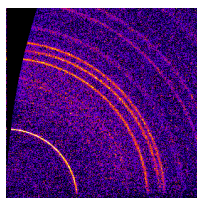
T. Antrack, M. Kroll, L. Merten, M. Albaladejo-Siguan, A. Hinderhofer, O. V. Konovalov, M. Jankowski, J. Benduhn, F. Schreiber, Y. Vaynzof, and K. Leo

Adv. Optical Mater. **2022**, *11*, 2201408

DOI: 10.1002/adom.202201408

Own Contributions: planning and supervision of X-ray measurements, data analysis.

Contributions by collaborators: Sample fabrication, all measurements, further ana-



lyses and manuscript writing.

X “Perovskite-Organic Tandem Solar Cells with Indium Oxide Interconnect”

K. O. Brinkmann, T. Becker, F. Zimmermann, C. Kreusel, T. Gahlmann, M. Theisen, T. Haeger, S. Olthof, C. Tückmantel, M. Günster, T. Maschwitz, F. Göbelsmann, C. Koch, D. Hertel, P. Caprioglio, F. Peña-Camargo, L. Perdigón-Toro, A. Al-Ashouri, L. Merten, A. Hinderhofer, L. Gomell, S. Zhang, F. Schreiber, S. Albrecht, K. Meerholz, D. Neher, M. Stolterfoht, and T. Riedl

Nature **2022**, *604*, 280

DOI: 10.1038/s41586-022-04455-0

Own Contributions: X-ray measurements and analysis.

Contributions by collaborators: Sample fabrication, all further measurements, analyses and manuscript writing.

XI “Unravelling the Structural Complexity and Photophysical Properties of Adamantyl-Based Layered Hybrid Perovskites”

F. Jahanbakhshi, M. Mladenović, E. Kneschaurek, L. Merten, M. C. Gélvez-Rueda, P. Ahlawat, Y. Li, A. Dučinskas, A. Hinderhofer, M. I. Dar, W. Tress, B. Carlsen, A. Ummadisingu, S. M. Zakeeruddin, F. Schreiber, A. Hagfeldt, F. Grozema, U. Roethlisberger, J. Milić, and M. Grätzel

J. Mater. Chem. A, **2020**, *8*, 17732

DOI: 10.1039/d0ta05022a

Own Contributions: analysis of X-ray data, writing of manuscript paragraphs.

Contributions by collaborators: Sample fabrication, all further measurements, analyses and manuscript writing.

XII “Optical Properties of Perovskite-Organic Multiple Quantum Wells”

T. Antrack, M. Kroll, M. Sudzius, C. Cho, P. Imbrasas, M. Albaladejo-Siguan, L. Merten, A. Hinderhofer, F. Schreiber, S. Reineke, Y. Vaynzof, and K. Leo

Adv. Sci. **2022**, *9*, 2200379

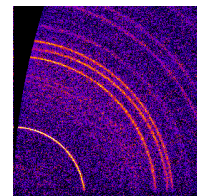
DOI: 10.1002/advs.202200379

Own contributions: Analysis of XRR data.

Contributions by collaborators: Sample fabrication, all further measurements, analyses and manuscript writing.

XIII “Elucidating Structure Formation in Highly Oriented Triple Cation Perovskite Films”

O. Telschow, N. Scheffczyk, A. Hinderhofer, L. Merten, E. Kneschaurek, F. Bertram, Q. Zhou, M. Löffler, F. Schreiber, F. Paulus, and Y. Vaynzof



APPENDIX A. LIST OF OWN PUBLICATIONS

Adv. Sci. **2023**, *10*, 2206325

DOI: 10.1002/advs.202206325

Own Contributions: Support in X-ray measurements and sample fabrication.

Contributions by collaborators: all further measurements, sample fabrication, analyses and manuscript writing.

XIV “Compact Sample Environment for In Situ X-ray Scattering During Spin-Coating”

E. Kneschaurek, A. Hinderhofer, B. Hofferberth, N. Scheffczyk, L. Pithan, P. Zimmermann, L. Merten, F. Bertram, and F. Schreiber

Rev. Sci. Instrum. **2023**, *94*, 063901

DOI: 10.1063/5.0149613

Own Contributions: Supporting role, review and editing of manuscript text.

Contributions by collaborators: setup development and construction, measurements, sample fabrication, analyses and manuscript writing.

XV “Minimizing Interfacial Recombination in 1.8 eV Triple-Halide Perovskites for 27.2 % Efficient All-Perovskite Tandems”

F. Yang, P. Tockhorn, A. Musienko, F. Lang, D. Menzel, R. Macqueen, E. Köhnen, K. Xu, S. Mariotti, D. Mantione, L. Merten, A. Hinderhofer, B. Li, D. R. Wargulski, S. P. Harvey, J. Zhang, F. Scheler, S. Berwig, M. Roß, J. Thiesbrummel, A. Al-Ashouri, K. O. Brinkmann, T. Riedl, F. Schreiber, D. Abou-Ras, H. Snaith, D. Neher, L. Korte, M. Stolterfoht, and S. Albrecht

Adv. Mater. **2023**, *36*, 2307743

DOI: 10.1002/adma.202307743

Own Contributions: X-ray measurements and analysis.

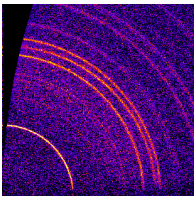
Contributions by collaborators: all further measurements, sample fabrication, analyses and manuscript writing.

i “How Crystallization Additives Govern Perovskite Grain Growth”

T. Maschwitz, L. Merten, F. Ünlü, A. Kotthaus, M. Majewski, F. Haddidi Barzoki, C. Kreusel, M. Theisen, P. Wang, M. Schiffer, H. Weidner, S. Schultheis, G. Marioth, D. Gidaszewski, Z. Julliev, E. Kneschaurek, V. Munteanu, F. Bertram, A. Jaffrès, J. He, N. Ashurov, C. M. Wolff, H. Grüninger, O. J. J. Ronsin, S. F. Kirsch, E. Unger, S. Mathur, A. Hinderhofer, F. Schreiber, K. O. Brinkmann, T. Riedl

In review

Own Contributions: X-ray measurements and analysis, planning and sample preparation, writing manuscript parts.



Contributions by collaborators: All further measurements, sample and device preparation, writing manuscript parts.

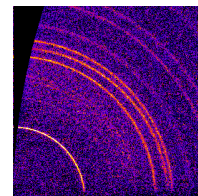
ii “Growth of Large Oriented MAPbI₃ Grains Independent of Crystallization Speed”

L. Merten, T. Maschwitz, F. Ünlü, A. Hinderhofer, E. Unger, K. O. Brinkmann, T. Riedl, F. Schreiber

In preparation

Own Contributions: X-ray measurements and analysis, planning and sample preparation, writing manuscript parts.

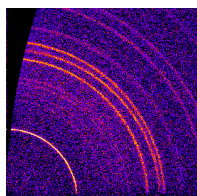
Contributions by collaborators: All further measurements, sample and device preparation, writing manuscript parts.



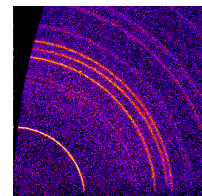
Appendix B

Abbreviations

Abbreviation	Meaning
1D, 2D, 3D	One/Two/Three dimensional
2H, 4H, 6H	Hexagonal polytypes with a repeating stacking sequence of 2/4/6 inequivalent hexagonal layers ⁹⁰
Å	Ångström, 10^{-10} m
α_c	Critical angle
α_i	Incidence angle
AFM	Atomic force microscopy
ALD	Atomic layer deposition
BNA ⁺	Benzylammonium (IUPAC name: Phenylmethanaminium)
DFT	Density functional theory
DJ	Dion-Jacobson
DMF	Dimethylformamide
DMSO	Dimehtylsulfoxide
E	Energy of the X-ray beam
E_g	Band gap energy
ETL	Electron transport layer
F	Structure factor
f	Atomic form factor
FA ⁺	Formamidinium (IUPAC name: Aminomethylideneazanium)
FBNA ⁺	(Perfluorobenzyl)ammonium (IUPAC name: (2,3,4,5,6-Pentafluorophenyl)methanaminium)
FEA ⁺	(2,3,4,5,6-Pentafluorophenyl)ethylammonium (IUPAC name: 2-(Perfluorophenyl)ethanaminium)

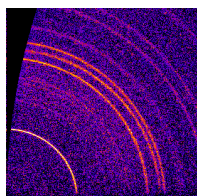


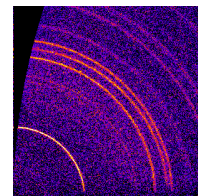
Abbreviation	Meaning
FF	Fill factor
FTIR	Fourier transform infrared spectroscopy
FTO	Flourinated tin oxide
FWHM	Full width at half maximum
GBL	γ -butyrolactone
GISAXS	Grazing incidence small angle X-ray scattering
GIWAXS	Grazing incidence wide angle X-ray scattering
(hkl)	Miller indices for diffraction planes
HTL	Hole transport layer
Im	Imidazolium
IPCE	Incident photon-to-current conversion efficiency
ITO	Indium tin oxide
J_{sc}	Short-circuit current
J-V	Current-voltage characeristic (J-V curve)
$\vec{k}$	Wave vector
k	Wave number, magnitude of wave vector
KPFM	Kelvin-Probe force microscopy
λ	Wavelength
M	Molarity
MA ⁺	Methylammonium (IUPAC name: Methanaminium)
mol	Mol, $6.022 \cdot 10^{23}$
mp-TiO ₂	Mesoporous TiO ₂
n	Number of lead halide layers in layered structures
$\tilde{n}$	Desired number of lead halide layers in layered structures by material composition
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
PCE	Power conversion efficiency
PDA ²⁺	1,4-Phenylenediammonium (IUPAC name: 1,4-Benzenediaminium)
PDEA ²⁺	1,4-Phenylenediethylammonium (IUPAC name: 2,2'-(1,4-Phenylene)diethanaminium)
PDMA ²⁺	1,4-Phenylenedimethylammonium (IUPAC name: 1,4-Phenylenedimethanaminium)
PEA ⁺	Phenylethylammonium (IUPAC name: 2-Phenylethanaminium)



APPENDIX B. ABBREVIATIONS

Abbreviation	Meaning
PL	Photoluminescence
PLQY	Photoluminescence quantum yield
$\vec{q}$	Scattering vector
q, q_r , also Q, Q_r	Magnitude of scattering vector
q_{xy}, q_z , also Q_{xy}, Q_z	Scattering vector components in in-plane and out-of-plane direction
RP	Ruddlesden-Popper
rpm	Rotations per minute
SDD	Sample-to-detector distance
SEM	Scanning electron microscopy
Spiro-OMeTAD	2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene
t	Tolerance factor (where indicated)
TFT	Trifluorotoluene
TPBi	1,3,5-tris(2-N-phenylbenzimidazolyl) benzene
UPS	Ultraviolet photoelectron spectroscopy
V_{oc}	Open-circuit voltage
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRR	X-ray reflectivity
Z	Atomic number
θ	Scattering angle
ω	Frequency

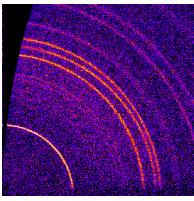




Appendix C

Experimental Details

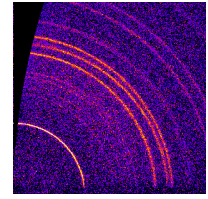
C.1 General Fabrication and Measurement Details for All Samples



C.1. GENERAL EXPERIMENTAL DETAILS

Table C.1: Experimental details for X-ray scattering experiments. SDD = sample-to-detector distance. All synchrotron-based experiments were performed under a nitrogen atmosphere, while the laboratory-based experiments were done under reduced pressure of 0.1 bar. The samples for Section 12.2 represent an exception since those were exposed to either dry or wet air during measuring repeatedly every 6 s. Incidence angles were $0-0.3^\circ$ for synchrotron-based measurements and below 0.5° for laboratory-based measurements. For real-time experiments, the integration time was 0.1 s. More details on measurements can be found in the respective publications listed in Table C.2. In-situ GIWAXS experiments were performed at DESY beamline P08³⁵⁹ in a dedicated sample environment (compare publication [XIII]).

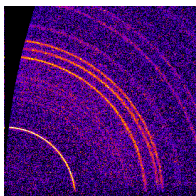
Section	Samples	Beamline	Beam Energy [keV]	Detector	SDD [mm]	Beam size [μm]
9.1	Mixed cation	ESRF ID10	22	Pilatus 300K	360	120x10
9.2	Gradient Cs^+ inclusion	DESY P08	18	PerkinElmer XRD1621		500x100
9.3	Imidazolium inclusion	ESRF ID10	22	Pilatus 300K	295	120x20
9.4	Halide segregation	DESY P23	12.974 – 13.974	Pilatus 1M	350	300x100
	Gas quenching real time growth	DESY P08	18	PerkinElmer XRD1621	700	500x200
	Lead acetate route real time growth	DESY P08	18	PerkinElmer XRD1621	700	400x100
10.1 - 10.3	Effect of TU additive	DESY P08	18	PerkinElmer XRD1621	700	300x100 - 500x200
11.1	PDMA-I-based layered structures	ESRF ID10	22	Pilatus 300K	295	120x20
11.2	PDMA-Br-based layered structures	xenocs XEUSS 2.0 laboratory beamline	8.04	Pilatus 300K	170	600
	PDMA-I-based structures on different substrates					600
	PDMA-I-based structures from different solvents	DESY P08	18	PerkinElmer XRD1621	700	500x100
11.3	DJ structures with different spacers and halides	ESRF ID10	22	Pilatus 300K	280	20x8.5
		DESY P08	18	PerkinElmer XRD1621	700	500x100
11.4	BNA-I based layered structures	xenocs XEUSS 2.0 laboratory beamline	8.04	Pilatus 300K	170	600
	Unannealed samples (PEA and BNA-based)	ESRF ID10	22	Pilatus 300K	280	20x8.5
	PEA-Br based layered structures	DESY P08	18	PerkinElmer XRD1621	700	300x100
	BNA-FACs based	DESY P23	13.226	Pilatus 1M	350	300x100
11.5	Layered structures with fluorinated spacers	xenocs XEUSS 2.0 laboratory beamline	8.04	Pilatus 300K	170	600
12.1	Antisolvent spraying vs dropping	ESRF ID10	22	Pilatus 300K	280	20x8.5
12.2	Controlled island formation					
13	Perovskite subcell	xenocs XEUSS 2.0 laboratory beamline	8.04	Pilatus 300K	170	600
	Organic subcell (small angle scattering)				1470	
	Interconnect + substrate layers	ESRF ID10	22	Pilatus 300K	280	20x8.5



APPENDIX C. EXPERIMENTAL DETAILS

Table C.2: Fabrication methods of perovskite thin film samples included in this thesis. References are provided in the last column for published details on the methods.

Section	Samples	Preparation method	Details found in
9.1	Multication	Antisolvent	Publication [I]
9.2	Gradient cesium inclusion	Antisolvent Surface treatment by crown-ether	Publication [II]
9.4	Mixed halides for segregation & real time growth	Lead acetate route	Publication [III]
	Mixed halides real time growth	Nitrogen gas quenching	
10.1 - 10.3	Effect of TU additive	Nitrogen gas quenching	Section C.3
10.2	TU additive for different quenching methods	Antisolvent	Section C.3
11.1 – 11.2	PDMA-based layered structures	Spin-coating	Publication [IV]
11.3	DJ structures with different spacers and halides	Spin-coating	Publication [V]
11.4	Layered structures with PEA^+ and BNA^+	Spin-coating	Publication [VI]
11.5	Layered structures with fluorinated spacers	Spin-coating	Publication [VII]
12.1	Antisolvent spraying vs dropping	Antisolvent	Publication [VIII]
12.2	Controlled island formation	Vacuum deposition	Publication [IX]
13	Perovskite-organic tandem solar cells	Nitrogen quenching (perovskite) ALD (interconnect) Spin-coating (organic layer)	Publication [X]



C.2 Experimental Details for Fabrication of CsPbBr₃ and CsSnBr₃ Thin Films in Section 7.4

CsPbBr₃ Thin Films

For the precursor solution for CsPbBr₃, lead bromide (PbBr₂, ultra dry, Alpha Aesar, 99.999 % purity) and CsBr (ultra dry, Sigma Aldrich, 99.999 % trace metal basis) were dissolved in anhydrous DMSO with a concentration of 0.33 mol/l and a molar ratio of CsBr:PbBr₂ of 2.75:1 by stirring over night at 60 °C and 1000 rpm. The solution was filtered through a 0.2 μm PTFE-filter before thin film deposition.

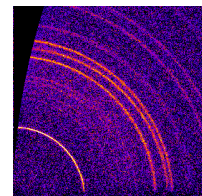
150 μl of the precursor ink were deposited onto a plasma cleaned glass substrate and spin-coated at 4000 rpm for 120 s. The thin films were annealed at 100 °C on a hotplate for 20 min.

Hot-pressing was applied to the annealed thin films at 100 bar and 150 °C for 30 min.

CsSnBr₃ Thin Films

CsBr and SnBr₂ were dissolved in a mixture of DMF and DMSO (1:4 v/v) in a concentration of 0.33 mol/l. Additionally, 5% (0.0165 mol/l) of SnF₂ were added to the precursor solution, which was stirred over night at 60 °C.

100 μl of the precursor ink were deposited onto a plasma cleaned glass substrate and spin-coated at 2000 rpm for 120 s, while 30 s before the end of spin-coating, nitrogen gas-quenching was applied.²⁸⁰ The thin films were annealed at 60 °C on a hotplate for 10 min. Hot-pressing was applied to the annealed thin films at up to 200 bar and 200 °C.



C.3 Experimental Details for Fabrication of Thin Films with Thiourea Additive in Chapter 10

These descriptions can be found in manuscript [i] as well, where additional details on further methods are listed.

Solution Preparation

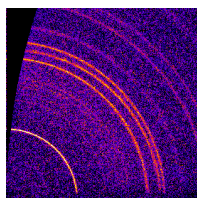
The precursor solution was prepared with a 7:3 volumetric ratio mixture of DMF (anhydrous, 99.8 %, Sigma-Aldrich) and NMP (anhydrous, 99.5 %, Sigma-Aldrich) by adding 1 mmol of methylammonium iodide (Greatcell Solar) and 1 mmol of lead iodide (ultra-dry from Alfa Aesar) per ml of solvent (mixture). In case thiourea was added later, the concentration of lead iodide was increased to 1.05 mmol/ml. The thiourea solution was prepared with 100 mg thiourea (Sigma-Aldrich) per ml of DMF.

For solutions to which thiourea has to be added later, the amount of DMF was reduced by 75 μ l per ml of solution. The solutions were then stirred for at least 4 h before shipping or further processing. In case of the usage of thiourea, 75 μ l of thiourea solution (which corresponds to 0.1 mol/l in the final solution) was added to the perovskite solution within 1 h before processing it. The perovskite solution was filtered through a 0.2 μ m PTFE-filter before thin film deposition.

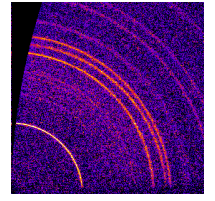
Thin Film Deposition

The deposition took place under nitrogen atmosphere. 17×17 mm glass substrates were used with an ITO-layer of 140 nm, which are cleaned preliminary to prevent particles from influencing layer formation. 180 μ l of solution were applied per substrate which was spin-coated at 3000 rpm for 120 s. Gas quenching was applied to control the crystallization process, as reported in reference [280]. The gas quenching was started 15–20 s after reaching the final rotational speed and continued for the rest of the spin-coating. For the samples produced by the antisolvent technique, the same spin-coating parameters were used, with the replacement of the nitrogen flow by dropping of 600 μ l (250 μ l in case of in-situ GIWAXS measurements) of the respective antisolvent (chlorobenzene or isopropanol) applying similar timing as in case of gas quenching.

After spin-coating, the sample was annealed for 10 minutes at 100 °C on a hot plate. During GIWAXS real time measurements, radiative heating was applied for the annealing step at about 130 °C for 5 min.



C.3. THIN FILMS WITH THIOUREA



Appendix D

Additional Data

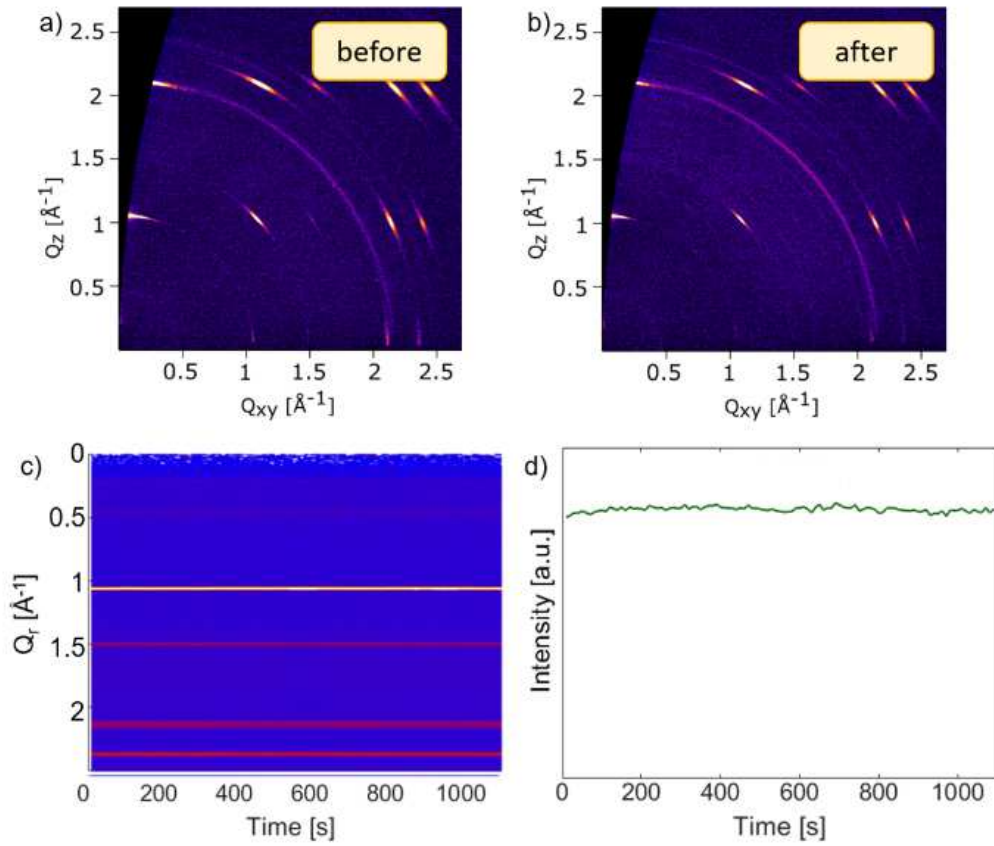


Figure D.1: GIWAXS reciprocal space maps of a MAPbBr_3 thin film (a) before and (b) after continuous exposure to X-rays for about 20 minutes. (c) Radial profiles of reciprocal space maps as a function of time. (d) Integrated intensity of the (100) perovskite diffraction signal as a function of time.

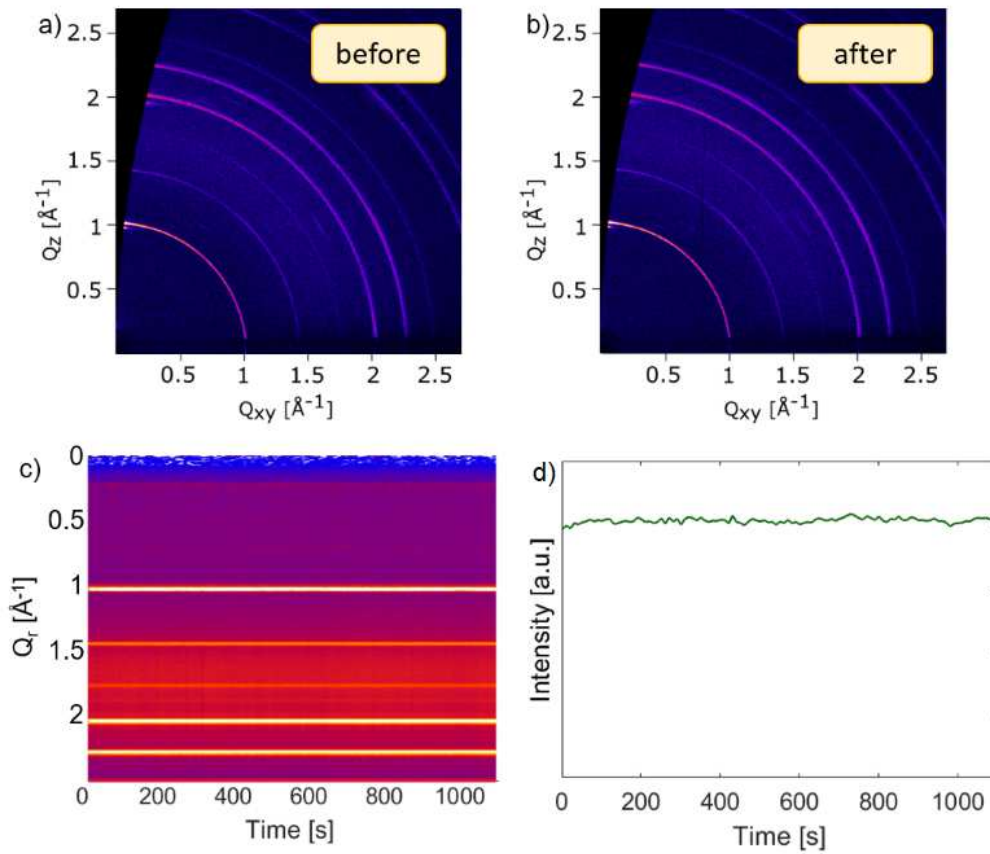
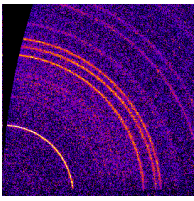


Figure D.2: GIWAXS reciprocal space maps of a $\text{MAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin film (a) before and (b) after continuous exposure to X-rays for about 20 minutes. (c) Radial profiles of reciprocal space maps as a function of time. (d) Integrated intensity of the (100) perovskite diffraction signal as a function of time. A small amount of the templating layered bromide-based phase (described in Section 9.4) is observed in both samples.

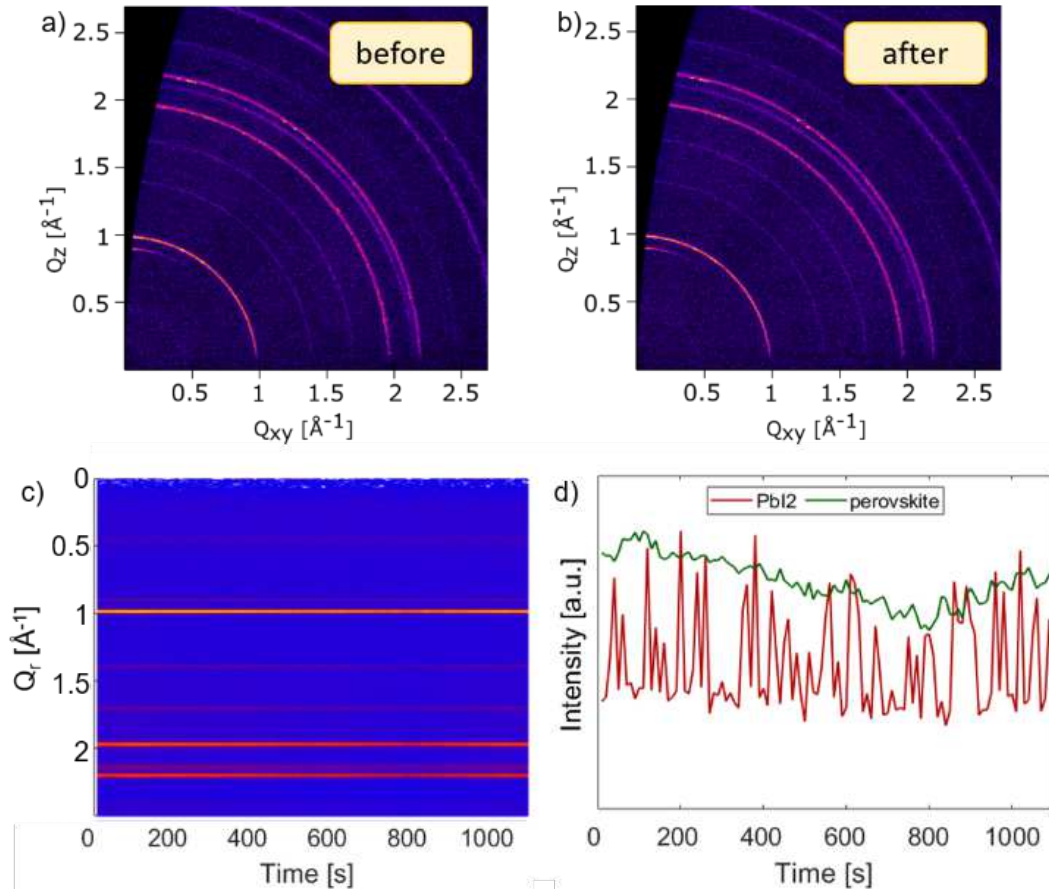
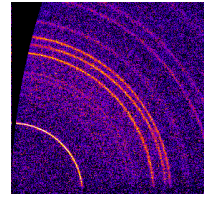


Figure D.3: GIWAXS reciprocal space maps of a FAPbI_3 thin film (a) before and (b) after continuous exposure to X-rays for about 20 minutes. (c) Radial profiles of reciprocal space maps as a function of time. (d) Integrated intensity of the (100) perovskite and PbI_2 diffraction signals as a function of time. Fluctuations in signal strength can be ascribed to slight variations in alignment.

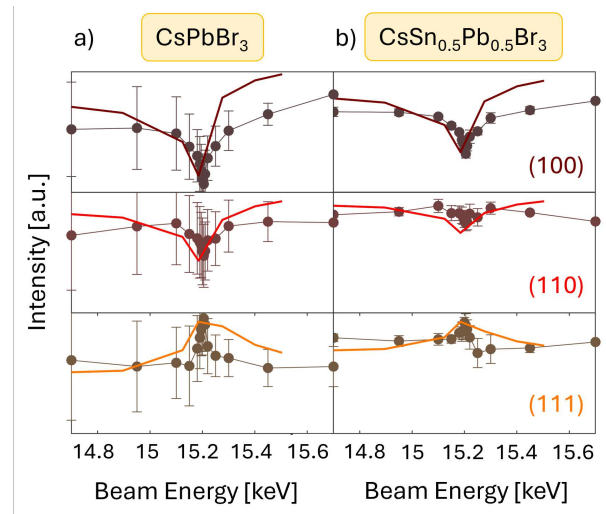
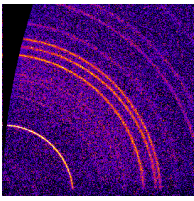


Figure D.4: Peak intensities of selected Bragg peaks as a function of beam energy around the lead L_{II} edge for (a) CsPbBr_3 and (b) $\text{CsSn}_{0.5}\text{Pb}_{0.5}\text{Br}_3$ thin films. Thick colored lines: simulated data,^{156,371} assuming a random mixture of tin and lead. Darker markers with thin lines: experimental data. Colored numbers in the graphs indicate Miller indices of the respective diffraction peaks.

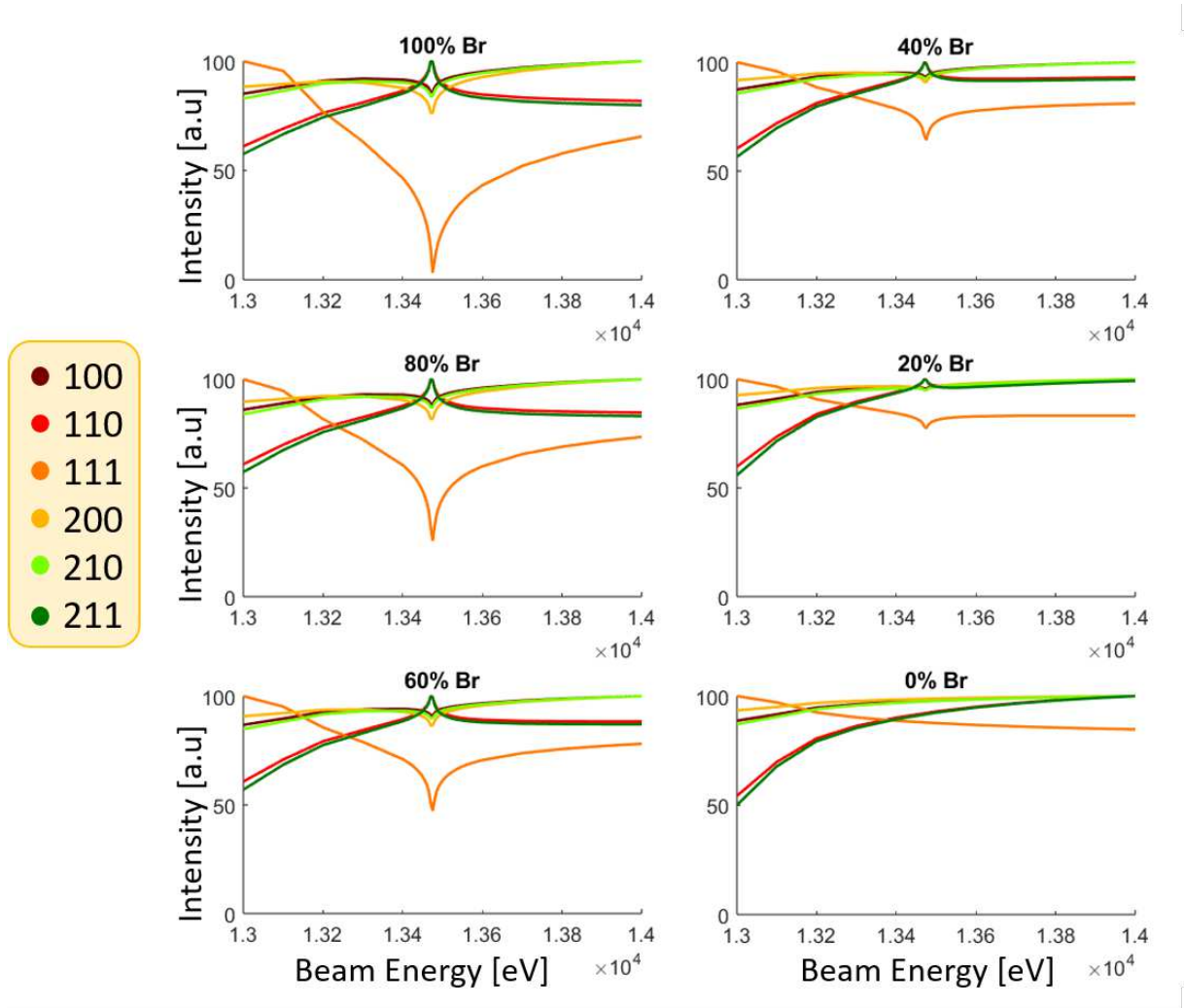
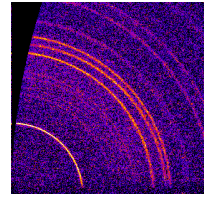


Figure D.5: Peak intensities of selected Bragg peaks as a function of beam energy around the bromide K-edge for MAPbBr_xI_{1-x} compositions for different mixing ratios and a randomly mixed model for bromide and iodide. Numbers in the legend give Miller indices of the respective diffraction signals.

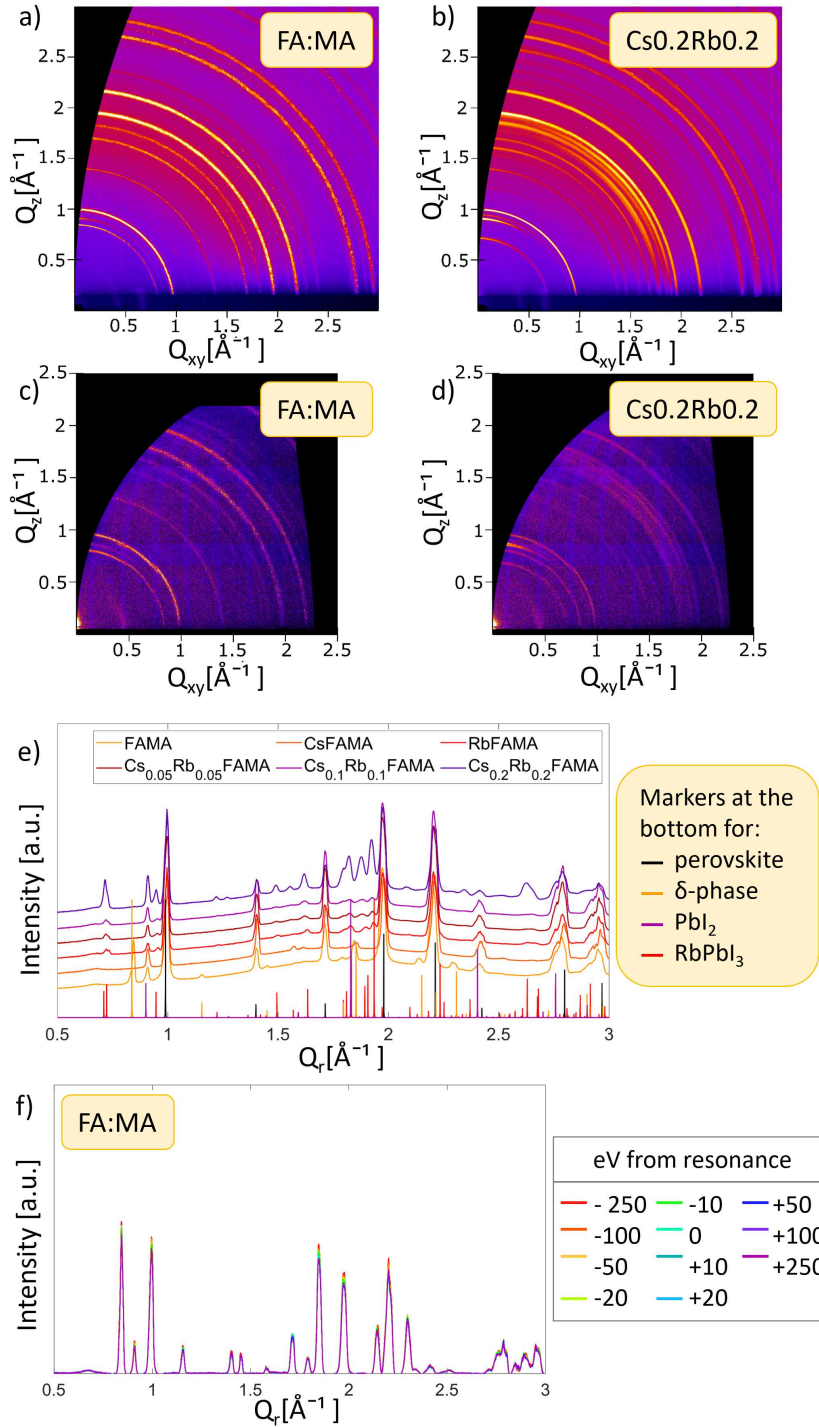
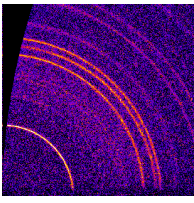


Figure D.6: Exemplary datasets for evaluating anomalous diffraction experiments on FA_{0.85}MA_{0.15}PbI₃ thin films with rubidium and cesium cation addition. GIWAXS reciprocal space maps at (a), (b) $E = 15.45$ keV; (c), (d) $E = 5.26$ keV and $\alpha_i = 1^\circ$. (e) Radial profiles at 15.45 keV with calculated peaks from literature,^{89,98,391} showing a mixture of phases. (f) Radial profiles of FA_{0.85}MA_{0.15}PbI₃ sample at different energies around the Pb L_{II} resonance edge at 15.2 keV.

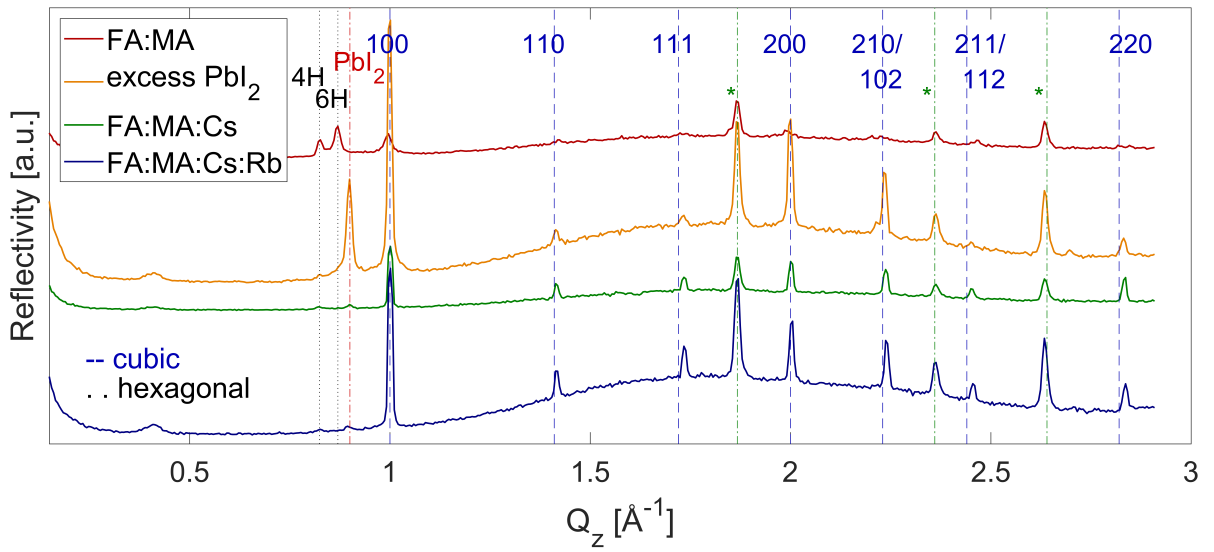
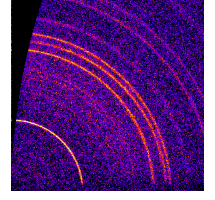
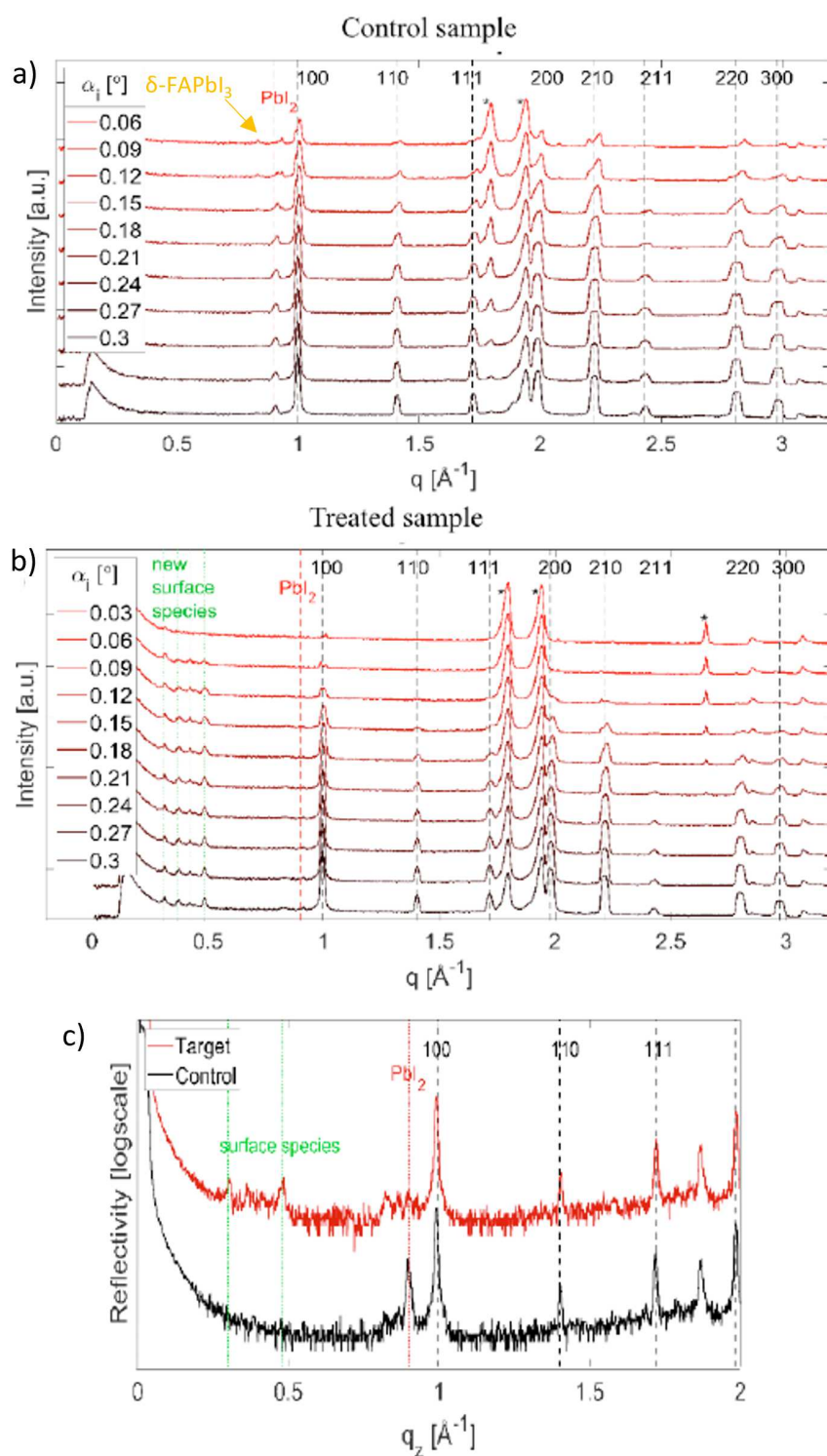


Figure D.7: X-ray reflectometry data of samples with different compositions, showing out-of-plane crystal structure. Peak indications after reported cubic perovskite structures and hexagonal polymorphs,⁸⁹ TiO_2 peaks originate from the substrate⁴⁸⁰ and are marked by green asterisks. In the double cation mixture containing formamidinium and methylammonium cations (red curve), additional hexagonal phase is visible, as well as a PbI_2 signal³⁹¹ in the sample containing excess PbI_2 (yellow curve). Addition of cesium and rubidium cations effectively suppresses hexagonal and PbI_2 phases (green and blue curves). Image taken from publication [I].



288

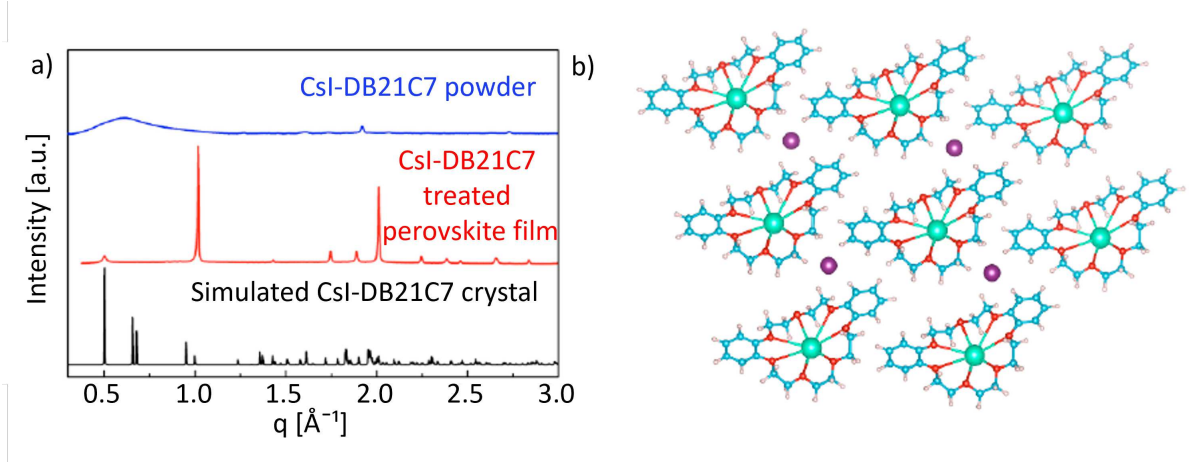
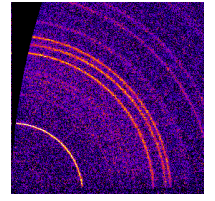


Figure D.9: (a) Powder X-ray diffraction patterns of the simulated CsI-dibenzo-21-crown-7 crystal, the CsI-dibenzo-21-crown-7 treated perovskite film and CsI-dibenzo-21-crown-7 powder. (b) Visualization of the DFT optimized crystal structure of CsI-dibenzo-21-crown-7. Color coding of species: Cesium-blue green, carbon-light blue, iodide-violet, oxygen-red and hydrogen-white. Image modified from publication [II].

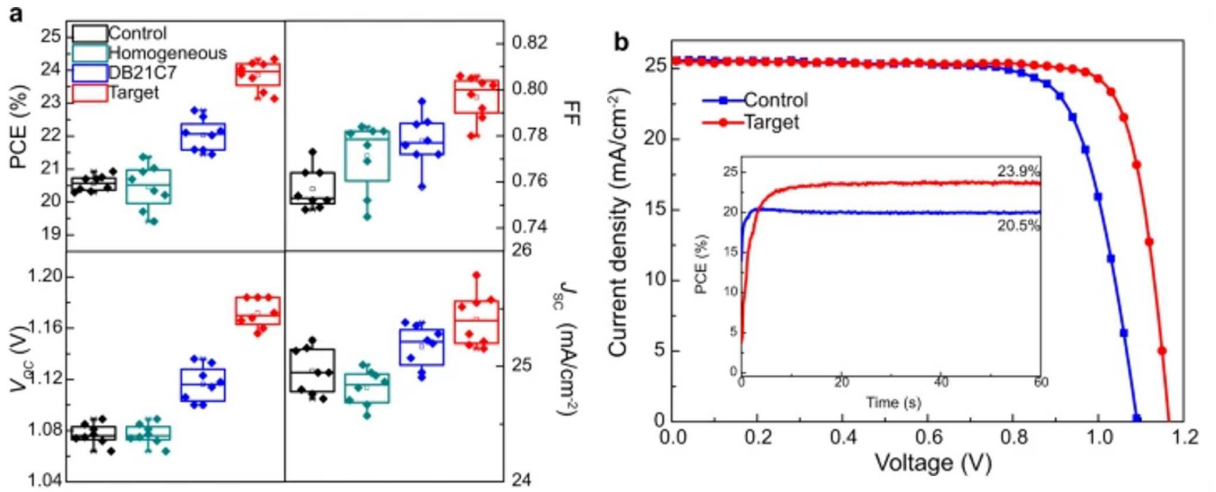


Figure D.10: (a) Photovoltaic metrics of FAPbI₃-based devices without cesium-doping (control), with homogeneous cesium-doping, after treatment with dibenzo-21-crown-7-CsI (target) and after just crown ether treatment. (b) Current-voltage (*J-V*) curves of the champion control and target solar cells. The inset shows the maximum power point tracking data. An anti-reflection coating was used for the champion devices. Image adjusted from publication [III].

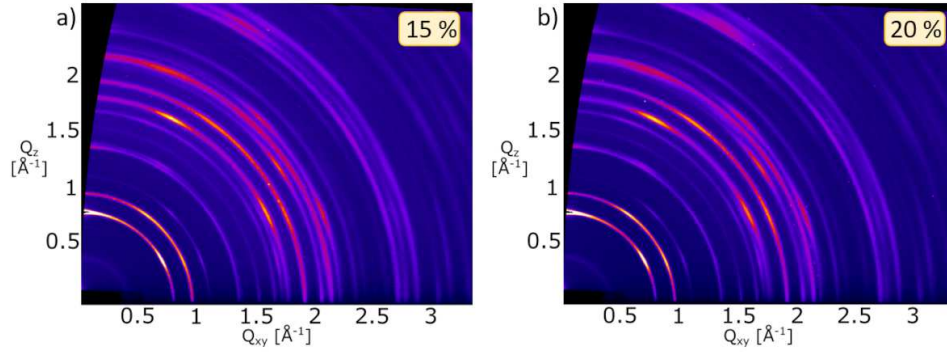
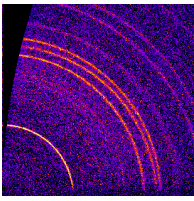


Figure D.11: GIWAXS reciprocal space maps of $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ thin films with addition of (a) 15 % and (b) 20 % of imidazolium.

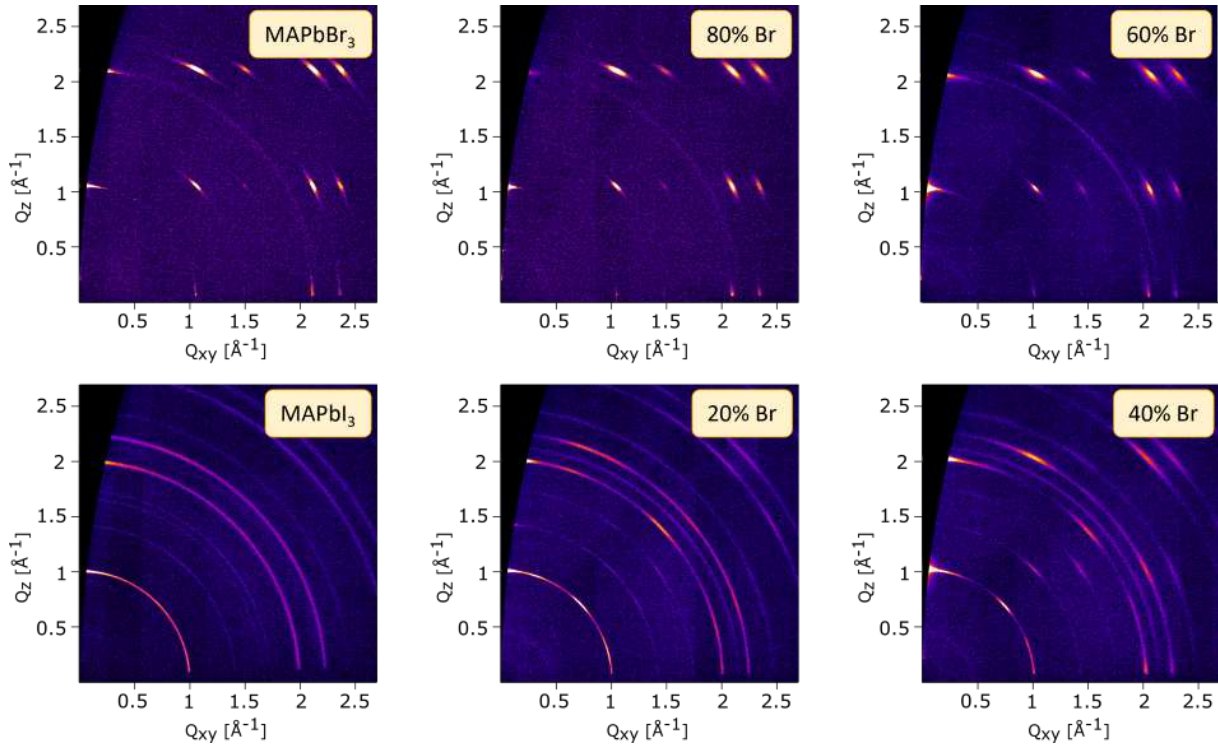


Figure D.12: GIWAXS reciprocal space maps of mixed halide $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin film samples fabricated via nitrogen-quenching. Incidence angle was 0.5° . Image taken from publication [III].

APPENDIX D. ADDITIONAL DATA

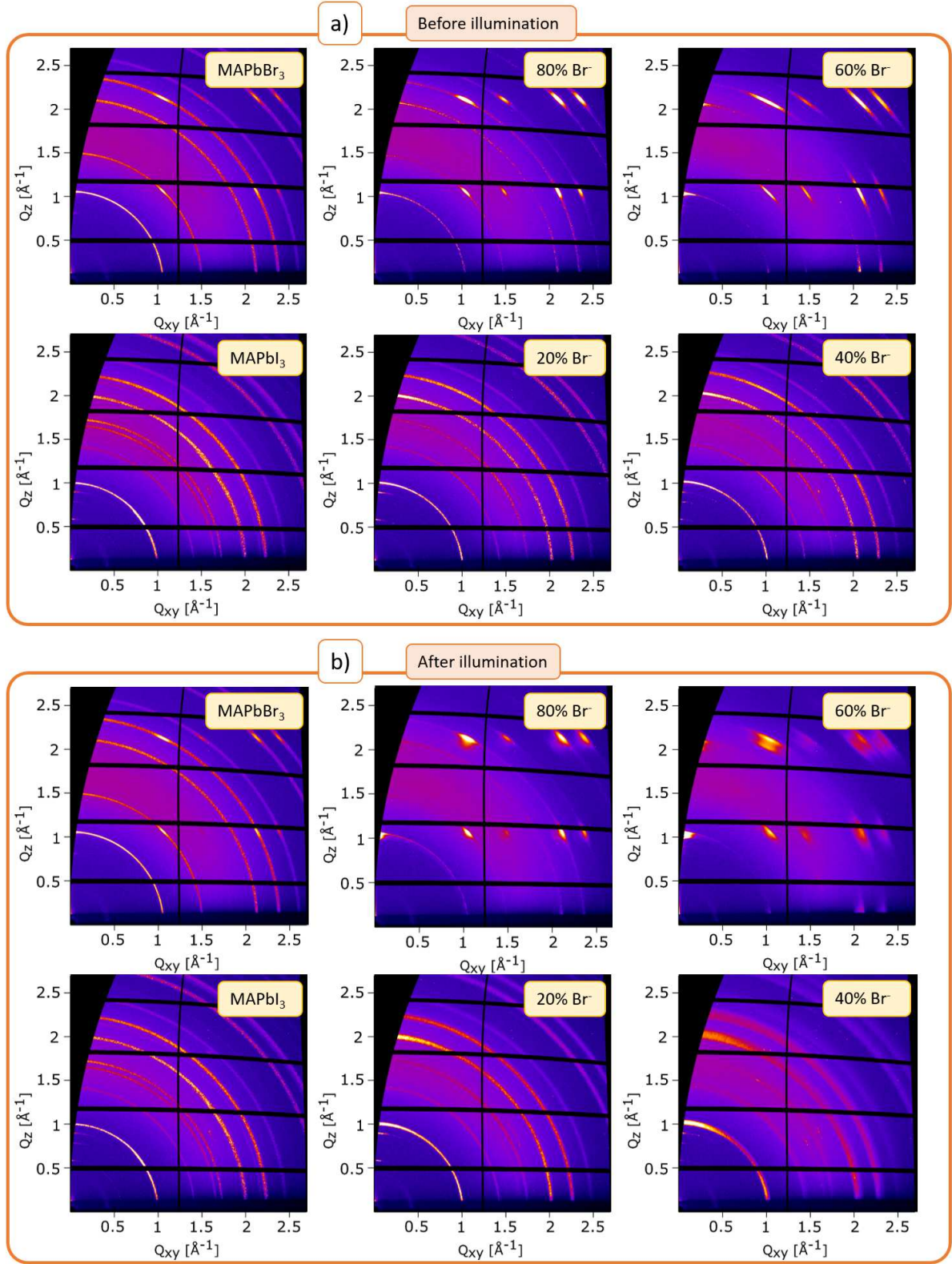
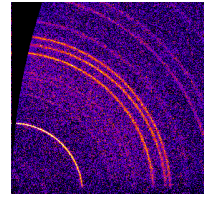


Figure D.13: GIWAXS reciprocal space maps of mixed halide $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin film samples fabricated via the lead acetate route (a) before and (b) after illumination. Incidence angle was 1° . Image taken from publication [III].

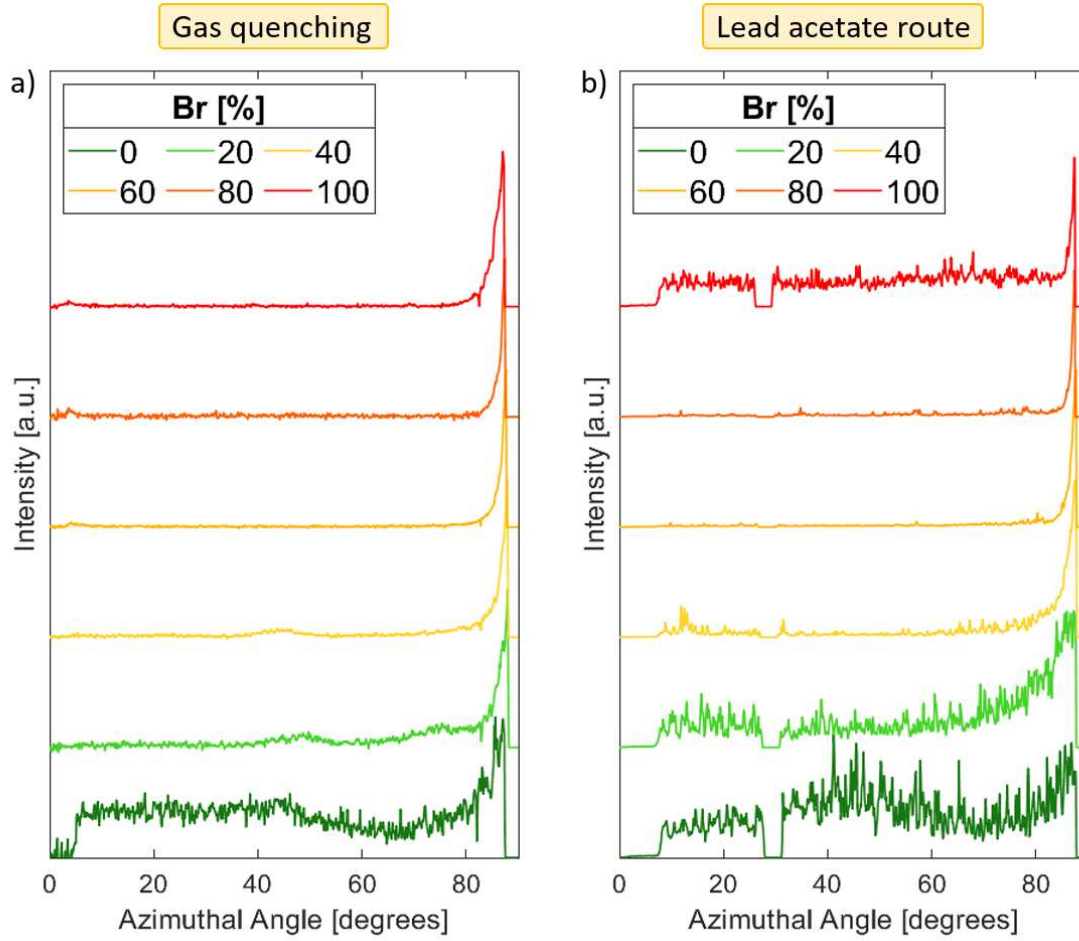
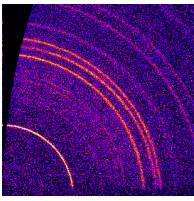


Figure D.14: Azimuthal profiles of the scattering intensity of the perovskite (100)/(110) diffraction peak at $q = 1\text{\AA}^{-1}$ for cubic/tetragonal structures, respectively. (a) Thin films fabricated via gas-quenching and (b) thin films fabricated by the lead acetate route. Image taken from publication [III].

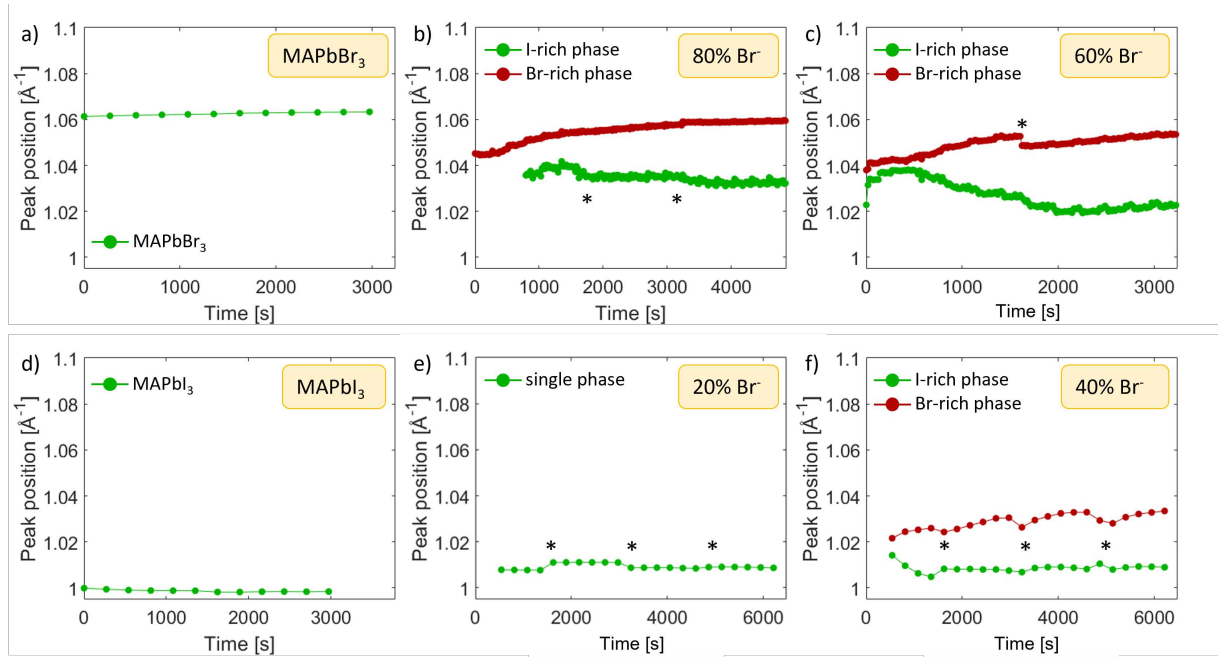
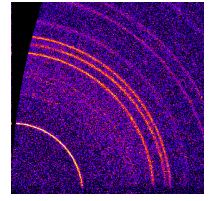


Figure D.15: Fitted peak positions of the (100) perovskite diffraction peak of the mixed halide MAPb(I_{1-x}Br_x)₃ thin film samples fabricated via the lead acetate route during illumination. Asterisks indicate a change in measuring position on the sample, leading to jump-like artefacts in the data. Image taken from publication [III].

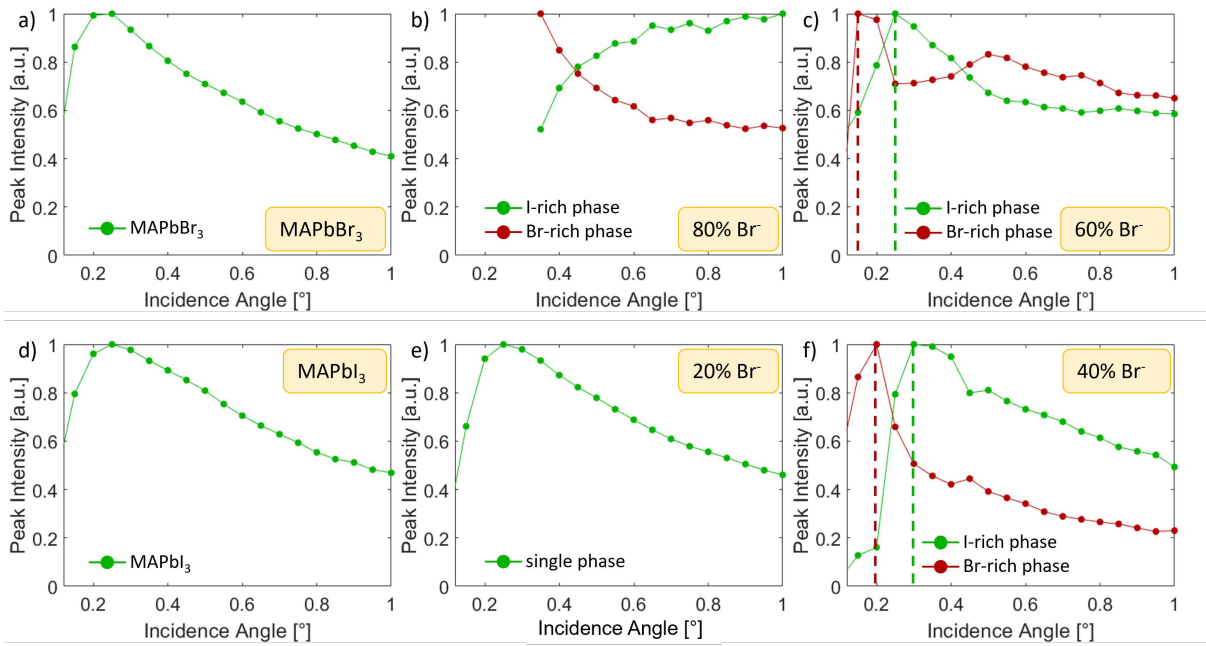
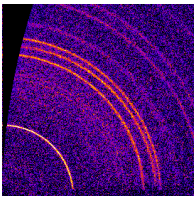


Figure D.16: Peak intensities as a function of incidence angle of the (100) perovskite diffraction peak of the mixed halide $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin film samples fabricated via the lead acetate route after illumination. Vertical dashed lines in Figures (c), (f) indicate angular intensity maxima of the different phases: A maximum at lower incidence angle, as for the bromide-rich phase (red curves) indicates location closer to the film surface, while compared to that the iodide-rich phase (green curves) exhibits its intensity maximum at slightly higher incidence angles, indicating its location further away from the surface. Generally, the lower the incidence angle, the smaller the probing depth, leading to increased surface sensitivity. Image taken from publication [III].

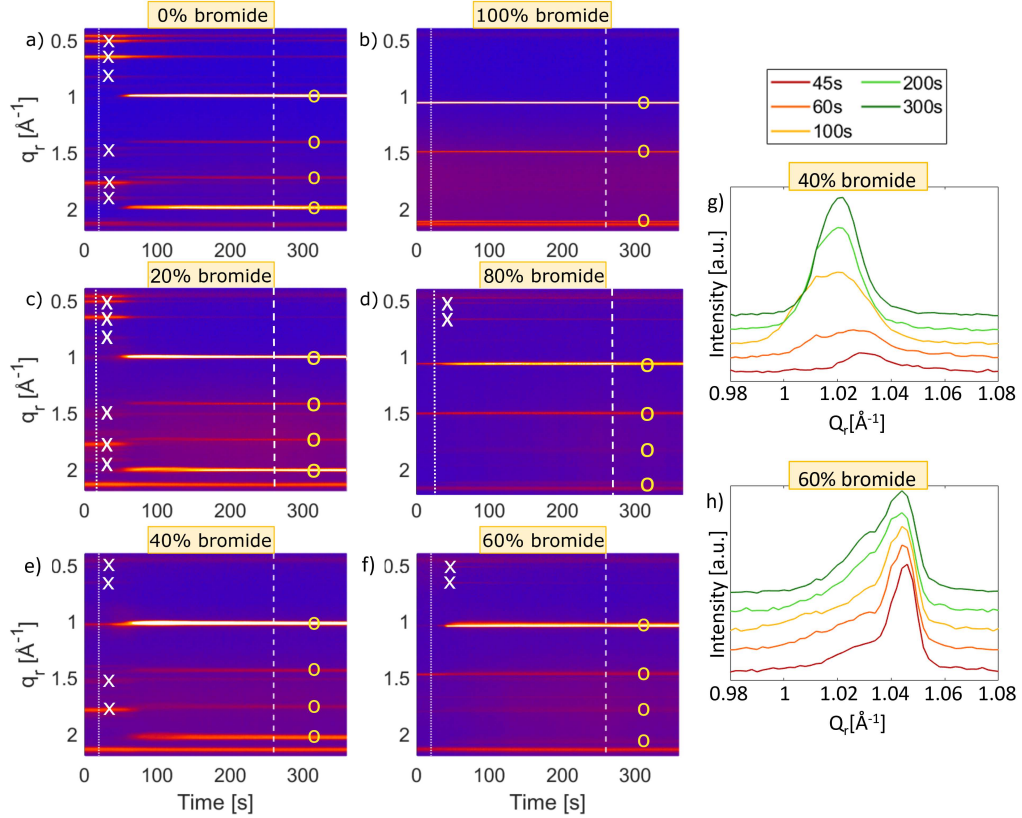
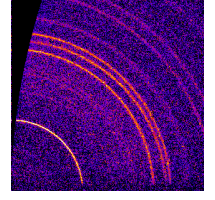


Figure D.17: Intensity maps from radial profiles of GIWAXS reciprocal space maps as a function of time during thermal annealing for $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin film samples fabricated via the N_2 gas quenching route. (a) 0 % bromide/pure MAPbI_3 , (b) 100 % bromide, (c) 20 % bromide, (d) 80 % bromide, (e) 40 % bromide, (f) 60 % bromide. White crosses mark $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ phase, while perovskite is marked with yellow circles. Vertical white dotted lines: start of heating; dashed lines: heat source turned off. (g), (h) Enlarged section of radial profiles at chosen instances in time during thermal annealing of samples with (g) 40 % bromide and (h) 60 % bromide content visualizing the shift of the diffraction signal to lower q upon iodide inclusion during thermal treatment. Image taken from publication [III].

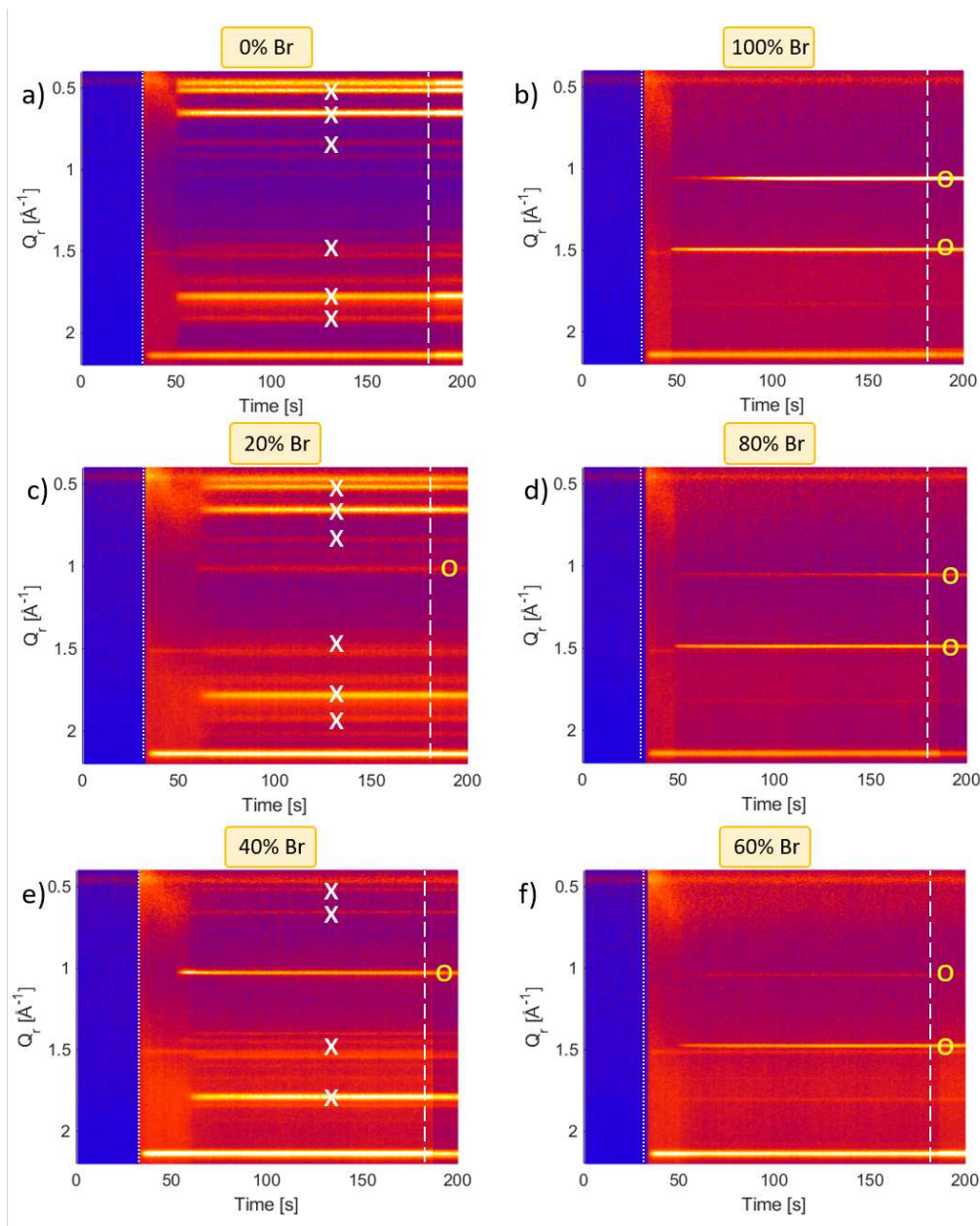
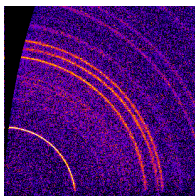


Figure D.18: Intensity maps from radial profiles of GIWAXS reciprocal space maps as a function of time during spin-coating for $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin film samples fabricated via the N_2 gas quenching route. (a) 0 % bromide/pure MAPbI_3 , (b) 100 % bromide, (c) 20 % bromide, (d) 80 % bromide, (e) 40 % bromide, (f) 60 % bromide. Spinning started at 30s (dotted vertical line) and stopped at 180s (dashed vertical line). White crosses mark the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ intermediate phase, yellow circles mark the perovskite phase. Image taken from publication [III].

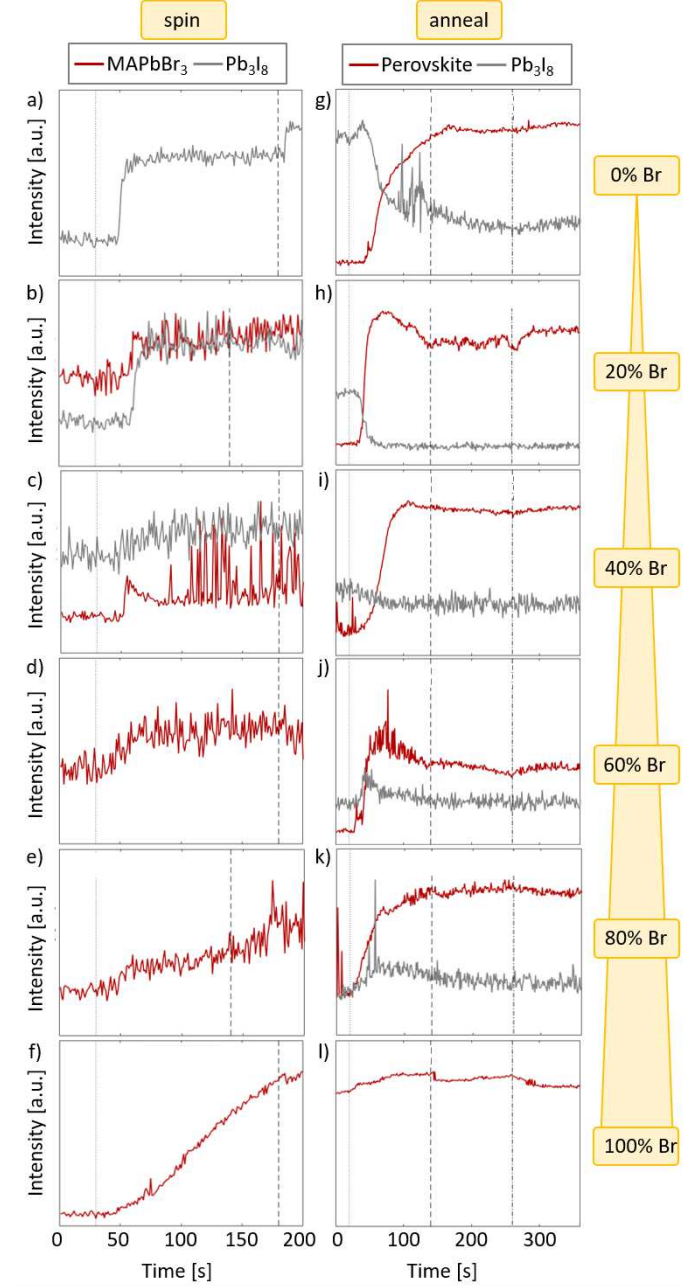
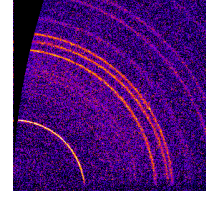


Figure D.19: Integrated peak intensities from radial profiles as a function of time during (a) – (f) spin-coating and (g) – (l) annealing for $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin film samples fabricated via the N_2 gas quenching route. (a), (g) 0 % bromide/pure MAPbI_3 , (b), (h) 20 % bromide, (c), (i) 40 % bromide, (d), (j) 60 % bromide, (e), (k) 80 % bromide, (f), (l) 100 % bromide. Legend colors apply for all samples, except during spin-coating the red curve marks the Br-rich perovskite phase and in the annealing data the mixed perovskite phase. A list of the signature peaks used for all phases can be found in Table D.1. Vertical dotted lines in (a) – (f): start of spinning; dashed lines: end of spinning. Vertical dotted lines in (g) – (l): start of heating; dashed lines: reduction of heating power; dot-dashed lines: heat source turned off. Pb_3I_8 in this case is short for the DMSO-based $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{DMSO}$ solvent complex. Image taken from publication [III].

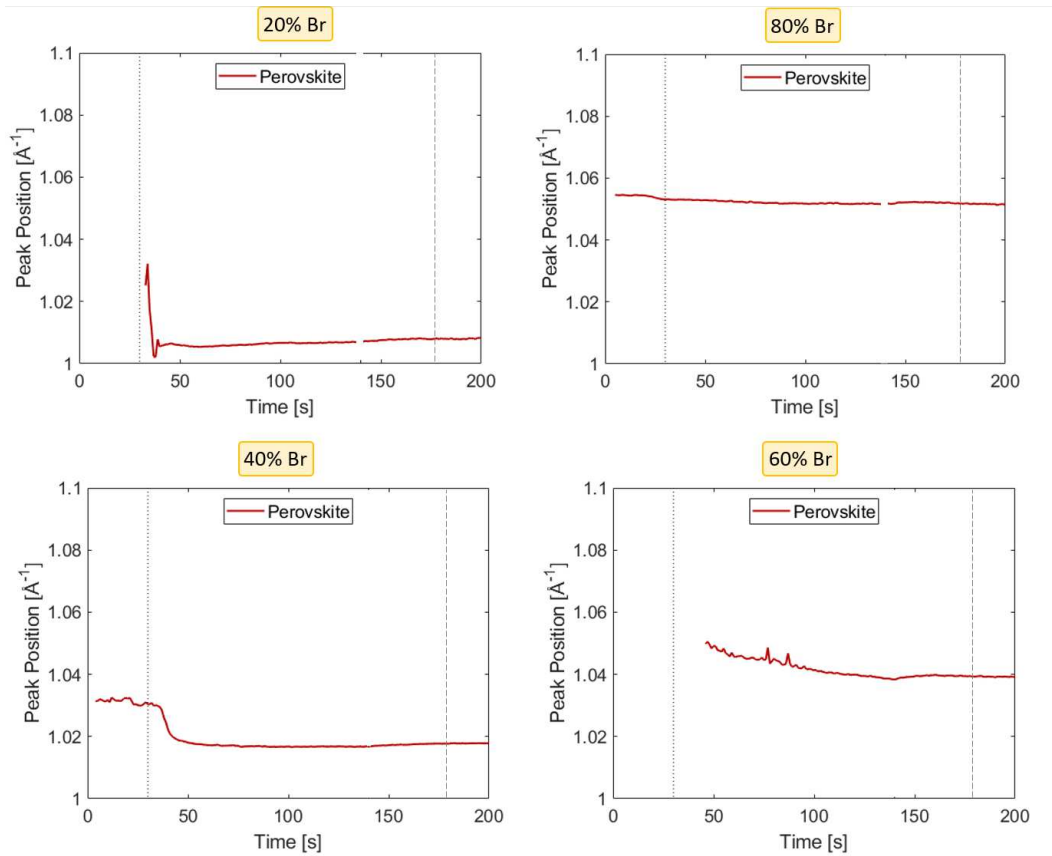
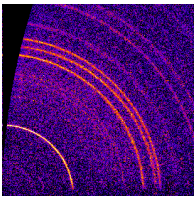


Figure D.20: Fitted peak positions from radial profiles of GIWAXS reciprocal space maps during annealing of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin film samples fabricated via the gas quenching route. Vertical dotted lines: start of spinning; dashed lines: end of spinning. Image taken from publication [III].

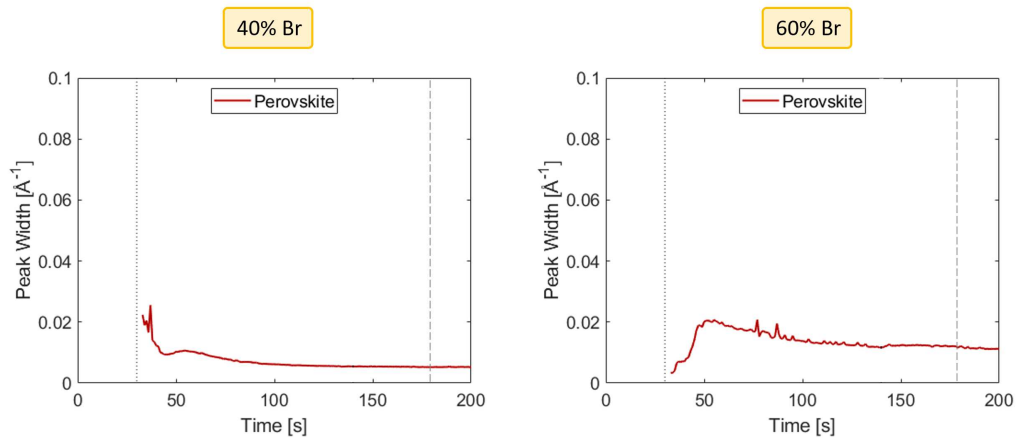
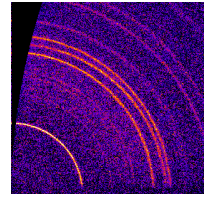


Figure D.21: Fitted peak widths from radial profiles of GIWAXS reciprocal space maps during annealing of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin film samples fabricated via the gas quenching route. (a) 40 % bromide, (b) 60 % bromide. Vertical dotted lines: start of spinning; dashed lines: end of spinning. Image taken from publication [III].

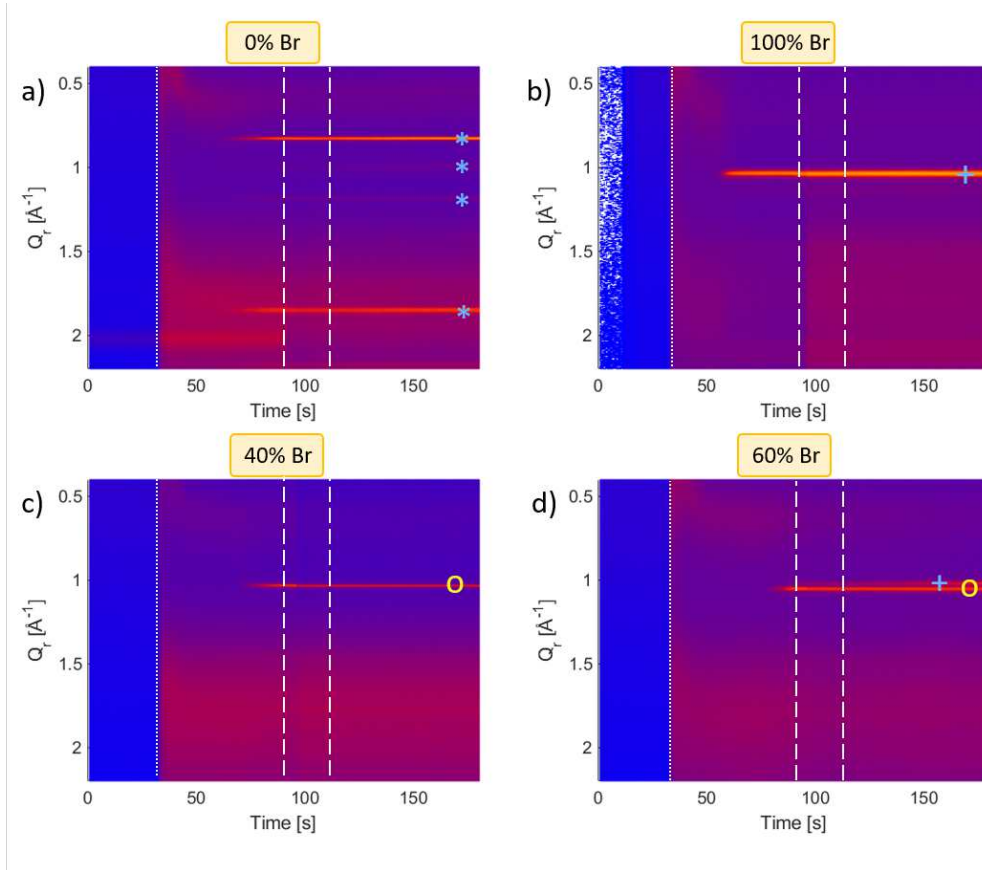
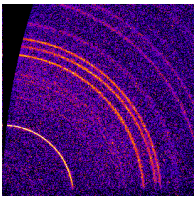


Figure D.22: Intensity maps from radial profiles of GIWAXS reciprocal space maps as a function of time during spin-coating for $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin film samples fabricated via the lead acetate route. (a) 0 % bromide/pure MAPbI_3 , (b) 100 % bromide, (c) 40 % bromide, (d) 60 % bromide. Spinning started at 30s (vertical dotted line) and stopped at 90s (first vertical dashed line) simultaneously with the start of a dry air flow, which stopped at 110s (second vertical dashed line). Yellow circles mark the perovskite phase, while blue asterisks mark hexagonal MAPbI_3 in (a) and blue plus signs mark layered MA_2PbBr_4 in (b) and (d). Image taken from publication [III].

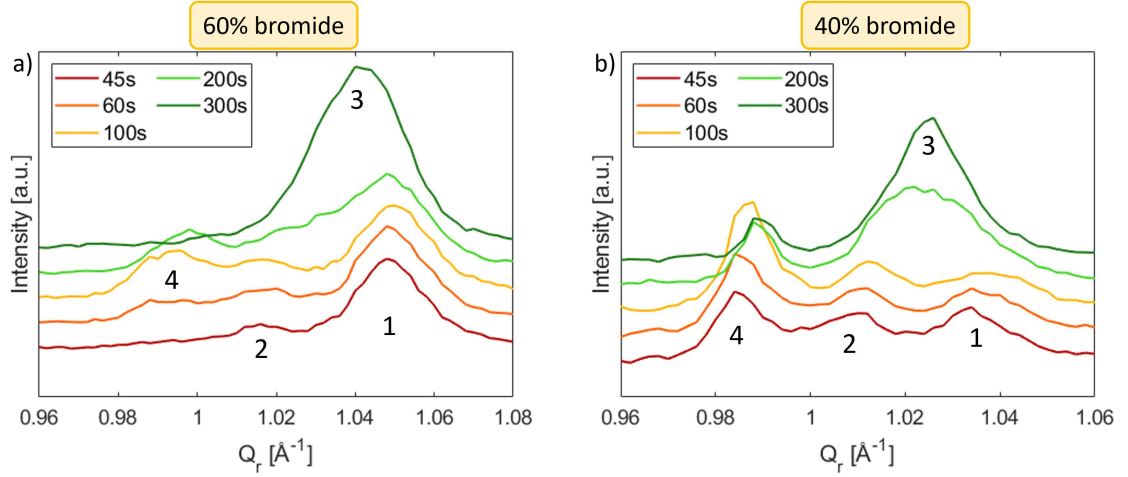
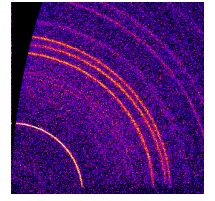


Figure D.23: Enlarged section of the radial profiles of GIWAXS reciprocal space maps, highlighting the region of the (100) perovskite diffraction signal during thermal annealing for thin films fabricated via the lead acetate route. (a) 40% bromide, (b) 60% bromide. Numbers in the plots indicate bromide-rich (1), iodide-rich (2) and mixed (3) perovskite phases and the layered MA_2PbBr_4 phase (4), in accordance with Figure 9.16. Image taken from publication [III].

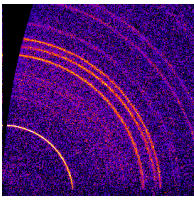


Table D.1: Peak positions of signature peaks used for tracking the phase compositions in Figures 9.15 and 9.17. The solvent in $(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{solvent}$ is DMSO^{102} in the gas quenching route and DMF^{18} in the lead acetate route.

Phase	$q [\text{\AA}^{-1}]$	hkl
Perovskite ^{35,53}	1 – 1.06	(100) ((002)/(110) for tetragonal MAPbI_3)
$(\text{MA})_2\text{Pb}_3\text{I}_8 \cdot 2\text{solvent}^{18,102}$	0.68 – 0.69	(022)
hex. $\text{MAPbI}_3^{154,155}$	0.82 – 0.83	(100)
layered $\text{MA}_2\text{PbBr}_4^{106}$	1.02 – 1.03	

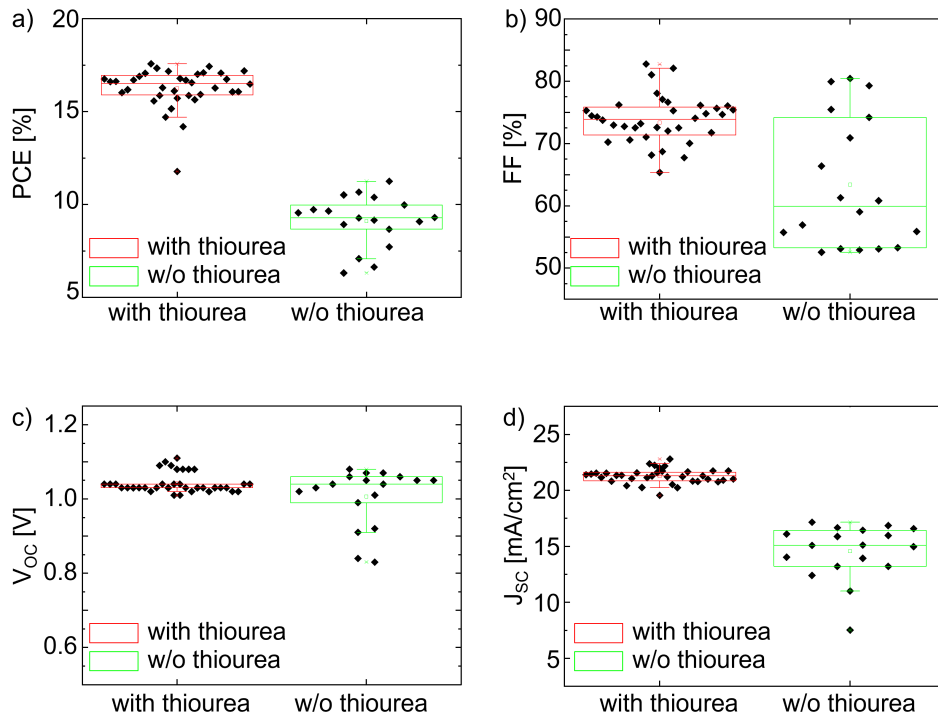


Figure D.24: Statistics of solar cells employing MAPbI_3 with and without 0.1 mol/l of thiourea additive. Upper and lower box ranges depict interquartile range (25 % – 75 %) with a median line in between. The whiskers show the ultimate data point inside yet another 1.5 interquartile range to identify outliers. (a) Power conversion efficiency (PCE), (b) fill factor, (c) open circuit voltage (V_{OC}) and (d) short circuit current J_{SC} .

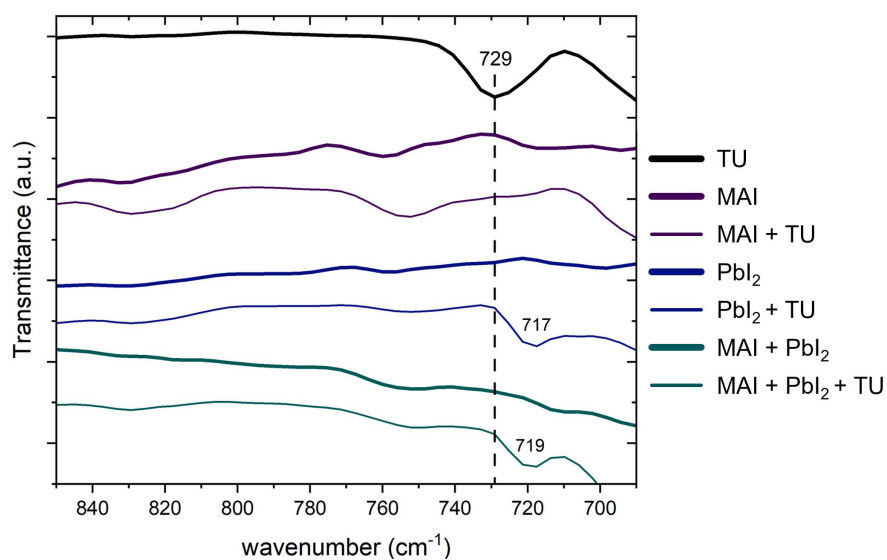
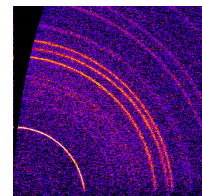


Figure D.25: Fourier transform infrared spectroscopy (FTIR) of the region around the C-S stretching vibration of thiourea in thin films of PbI_2 , MAI, MAPbI_3 with and without thiourea addition.

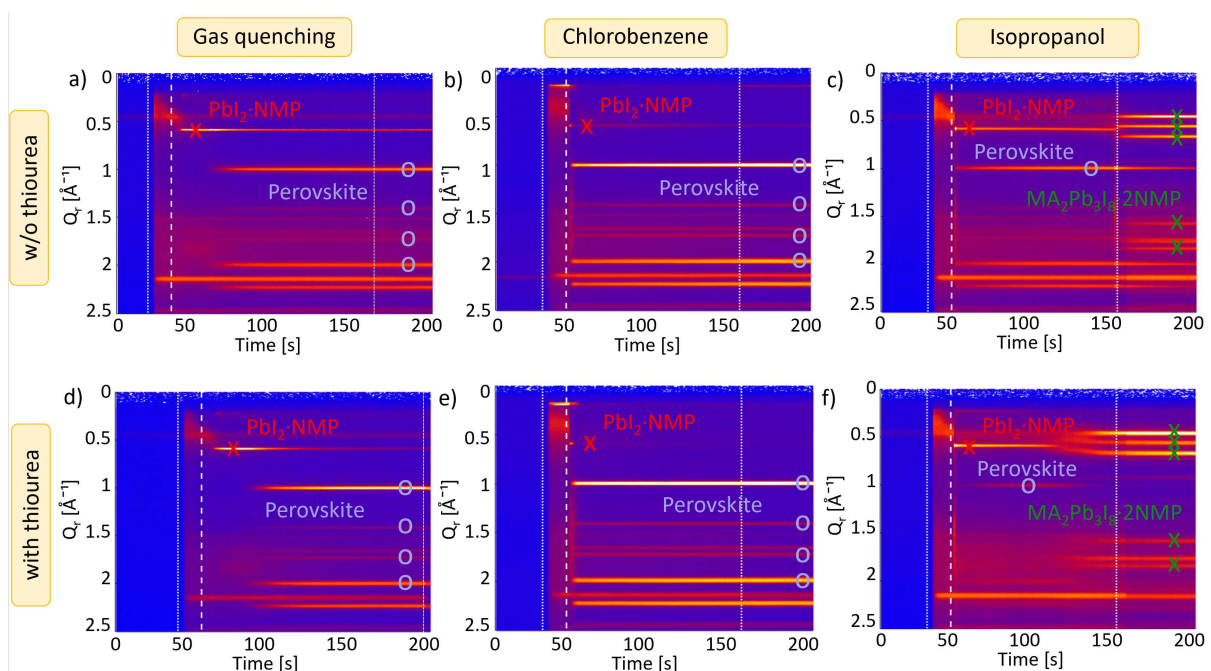
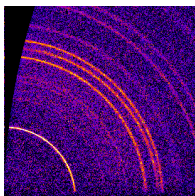


Figure D.26: GIWAXS radial intensities as a function of time during spin-coating of MAPbI_3 employing different quenching methods without and with addition of thiourea to the precursor solution. Vertical dotted lines indicate start and end of the spin-coating, while dashed lines indicate start of the quenching procedure. Red crosses mark the $\text{PbI}_2 \cdot \text{NMP}$ phase, blue circles indicate the perovskite phase and green crosses mark the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{NMP}$ phase.

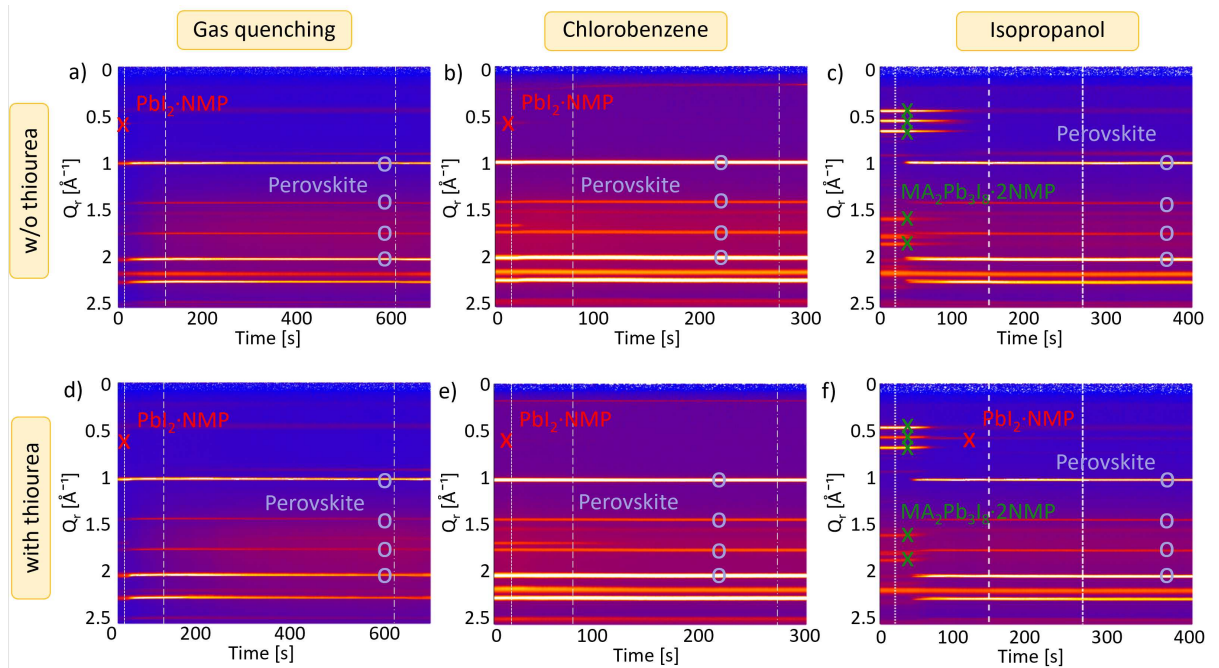
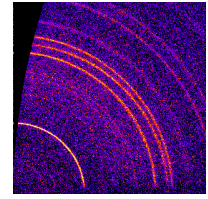


Figure D.27: GIWAXS radial intensities as a function of time during annealing of MAPbI_3 employing different quenching methods without and with addition of thiourea to the precursor solution. Vertical dotted lines indicate start of heating, while dashed lines indicate a reduction of heating power and dot-dashed lines the end of thermal treatment. Red crosses mark the $\text{PbI}_2 \cdot \text{NMP}$ phase, blue circles indicate the perovskite phase and green crosses mark the $\text{MA}_2\text{Pb}_3\text{I}_8 \cdot 2\text{NMP}$ phase.

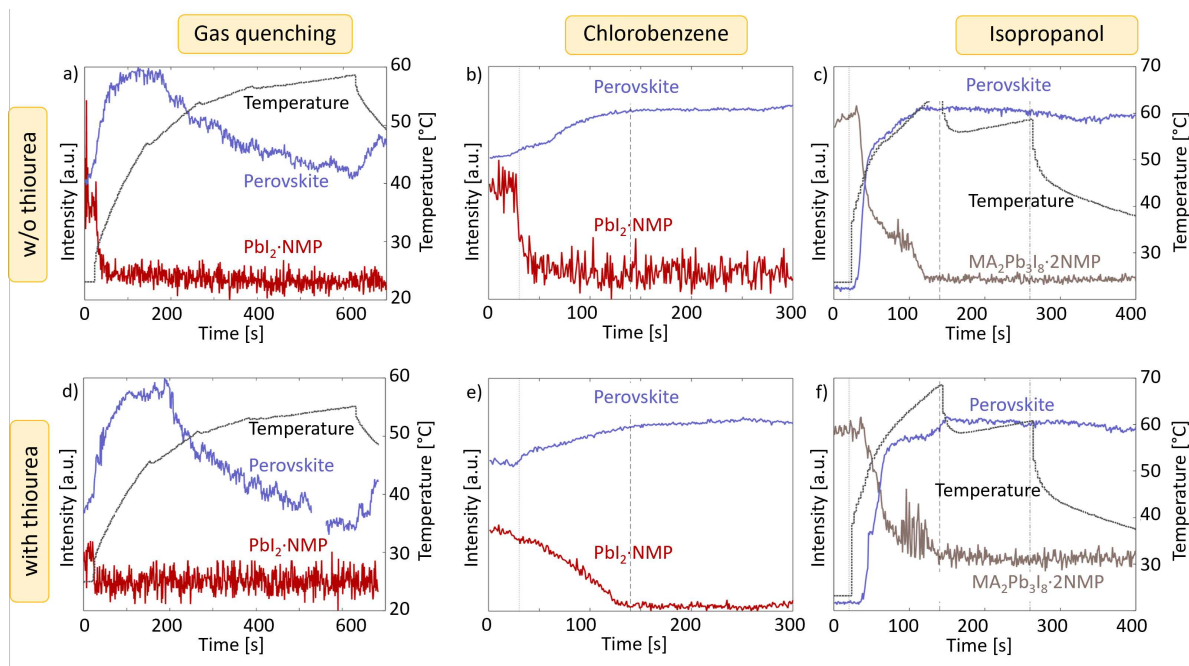
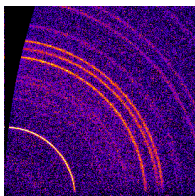


Figure D.28: Integrated GIWAXS diffraction signal intensities from distinct crystal phases as a function of time during thermal annealing of MAPbI_3 employing different quenching methods without and with addition of thiourea to the precursor solution. The signals used for each phase can be found in Table D.2.

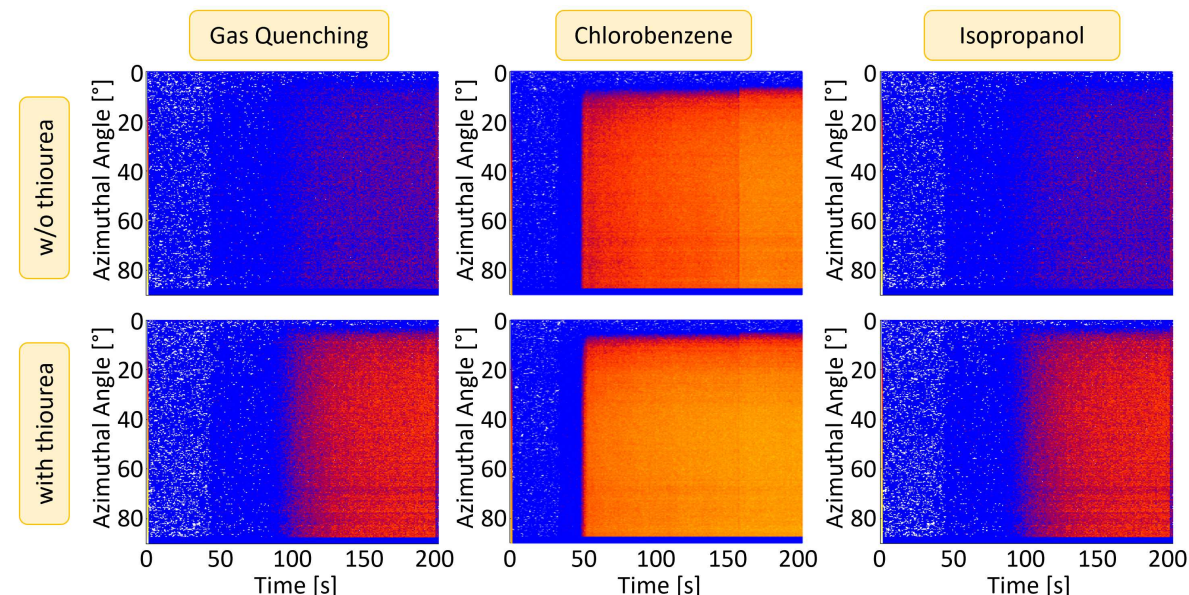


Figure D.29: Azimuthal intensities of the (110) perovskite diffraction signal as a function of time during spin-coating of MAPbI_3 employing different quenching methods without and with addition of thiourea to the precursor solution.

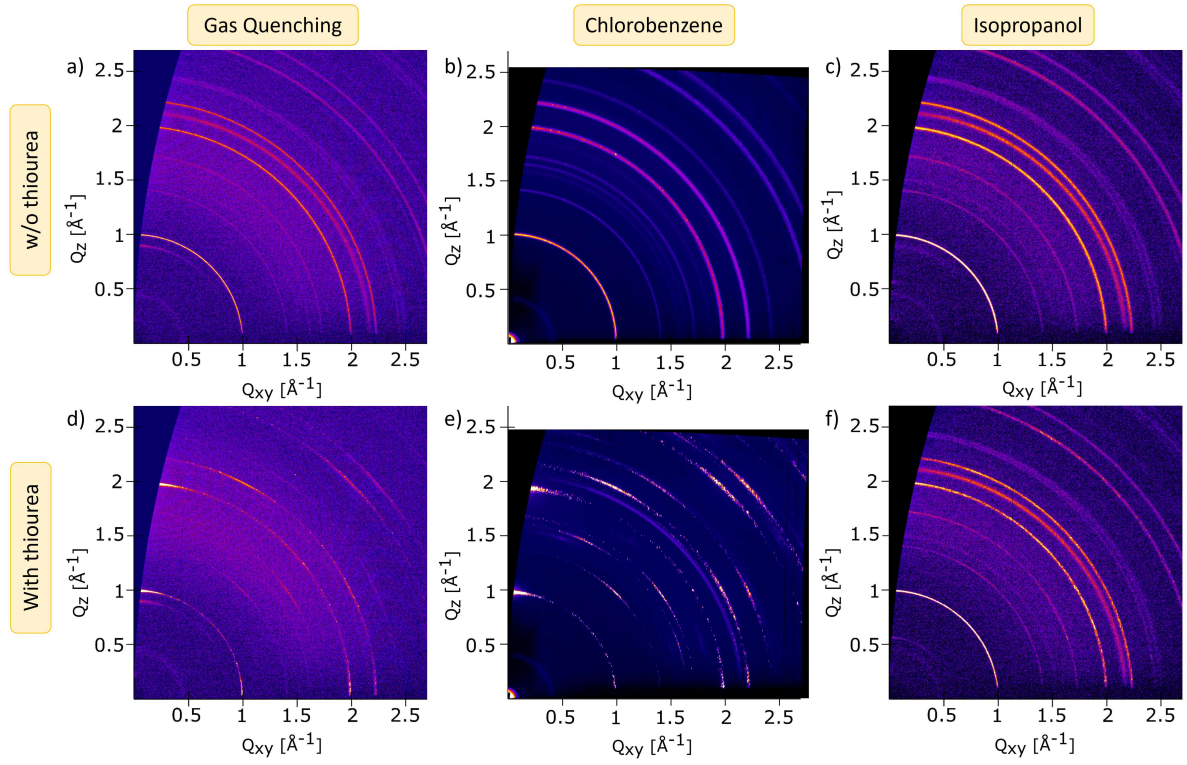


Figure D.30: Reciprocal space maps obtained by GIWAXS of final MAPbI_3 thin films fabricated by different quenching methods without and with addition of thiourea to the precursor solution.

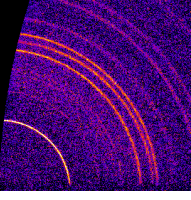


Table D.2: Peak positions of signature peaks used for tracking the phase compositions in Figure 10.10.

Phase	q [$\text{\AA}^{-1}$]	hkl
Perovskite ^{35, 53}	~ 1	(002)/(110)
$(MA)_2Pb_3I_8 \cdot 2NMP$ ^{18, 102}	0.67	(022)
$PbI_2 \cdot NMP$ ¹⁰⁰	0.59/1.65	(020)/(111)

Table D.3: Peak positions of signature peaks used for tracking the phase compositions in Figures 10.14, 10.17 and 10.19.

Phase	q [$\text{\AA}^{-1}$]	hkl
Perovskite ^{35, 53}	1 – 1.06	(100) ((002)/(110) for tetragonal $MAPbI_3$)
$(MA)_2Pb_3I_8 \cdot 2NMP$ ^{18, 102}	0.5 – 0.58	(012)/(021)
$PbI_2 \cdot NMP$ ¹⁰⁰	0.58 – 0.59	(020)
FAI- $PbI_2 \cdot xNMP$	0.59 – 0.63	
δ -FAPbI ₃ ⁸⁹	0.8 – 0.86	(100)

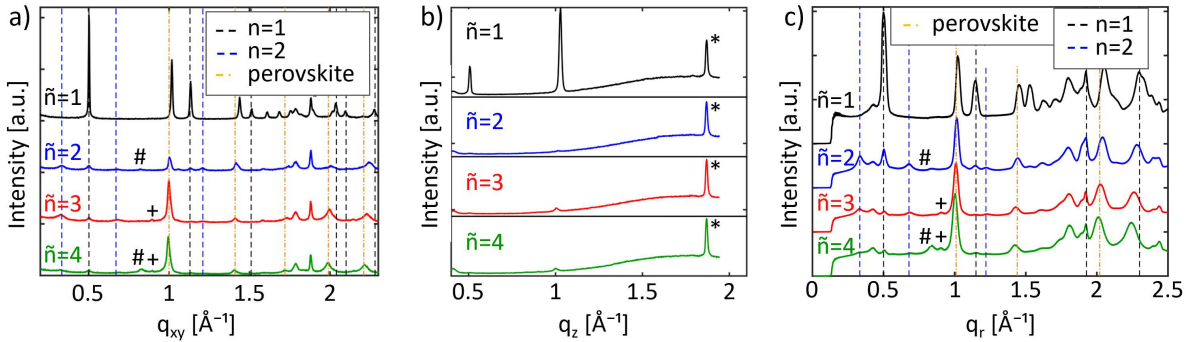


Figure D.31: (a) In-plane diffraction and (b) XRR data as well as (c) radial intensity of GIWAXS reciprocal space maps at $\alpha_i = 0.1^\circ$ for perovskite thin films based on $(PDMA)FA_{n-1}Pb_nI_{3n+1}$ with $\tilde{n} = 1$ (black), $\tilde{n} = 2$ (blue), $\tilde{n} = 3$ (red) and $\tilde{n} = 4$ (green) compositions on FTO/mp-TiO₂ substrates. Peak indications based on literature reports.^{89, 480} Vertical lines indicate peak positions of the respective phases, while * marks the substrate peak, # denotes additional hexagonal phase, and + is for PbI_2 . Images taken from publication [IV].

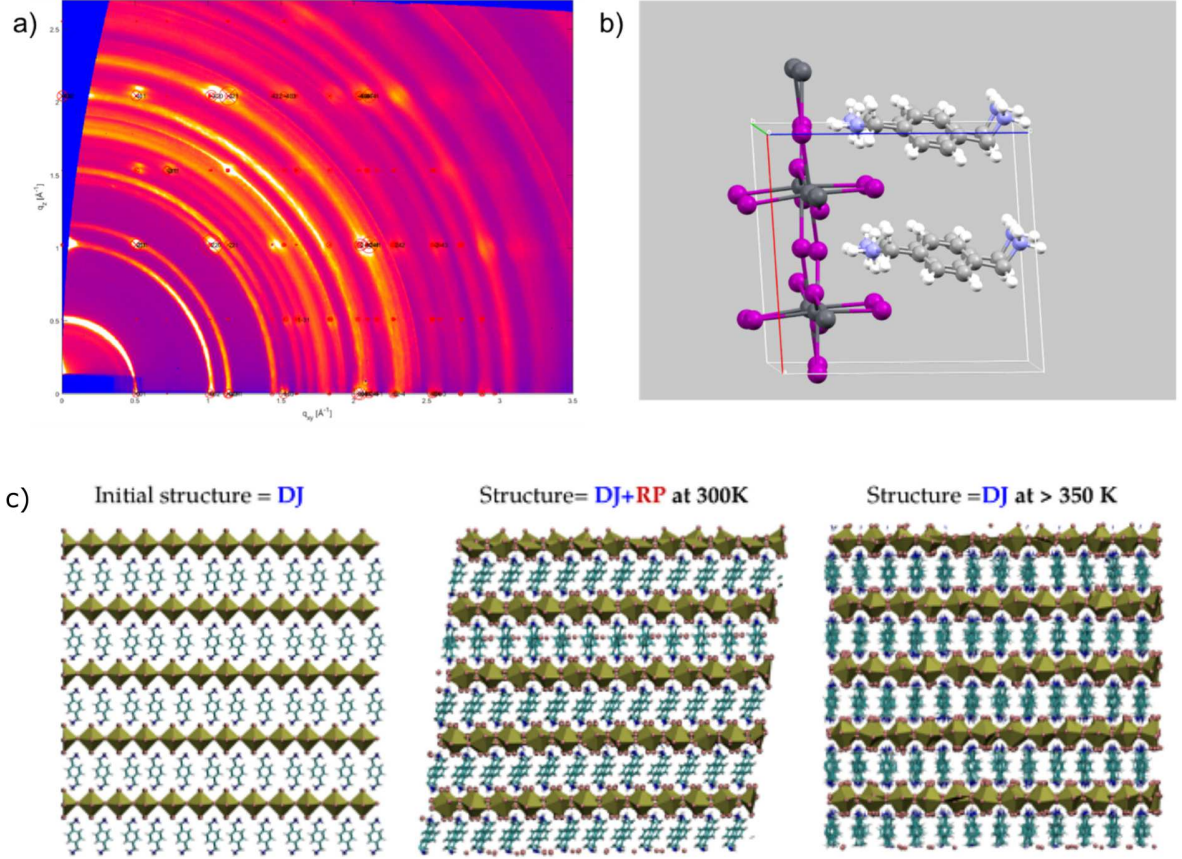
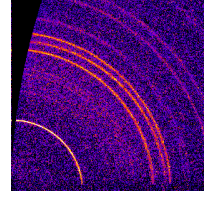


Figure D.32: (a) Comparison of the simulated pattern from the fitted unit cell to experimental data for $\tilde{n} = 1$ perovskite compositions. (b) Visualization of the unit cell for the $n = 1$ phase. (c) Structural changes with temperature. On the left is the initial geometry, middle shows the intermediate phase and on the right is the final relaxed structure. Lead cations are shown with golden spheres, iodide is displayed with pink spheres, and Pb-I octahedra are shown in gold. PDMA²⁺ is illustrated with a ball-and-sticks model. The images are generated with VMD. Images taken from publication [IV].

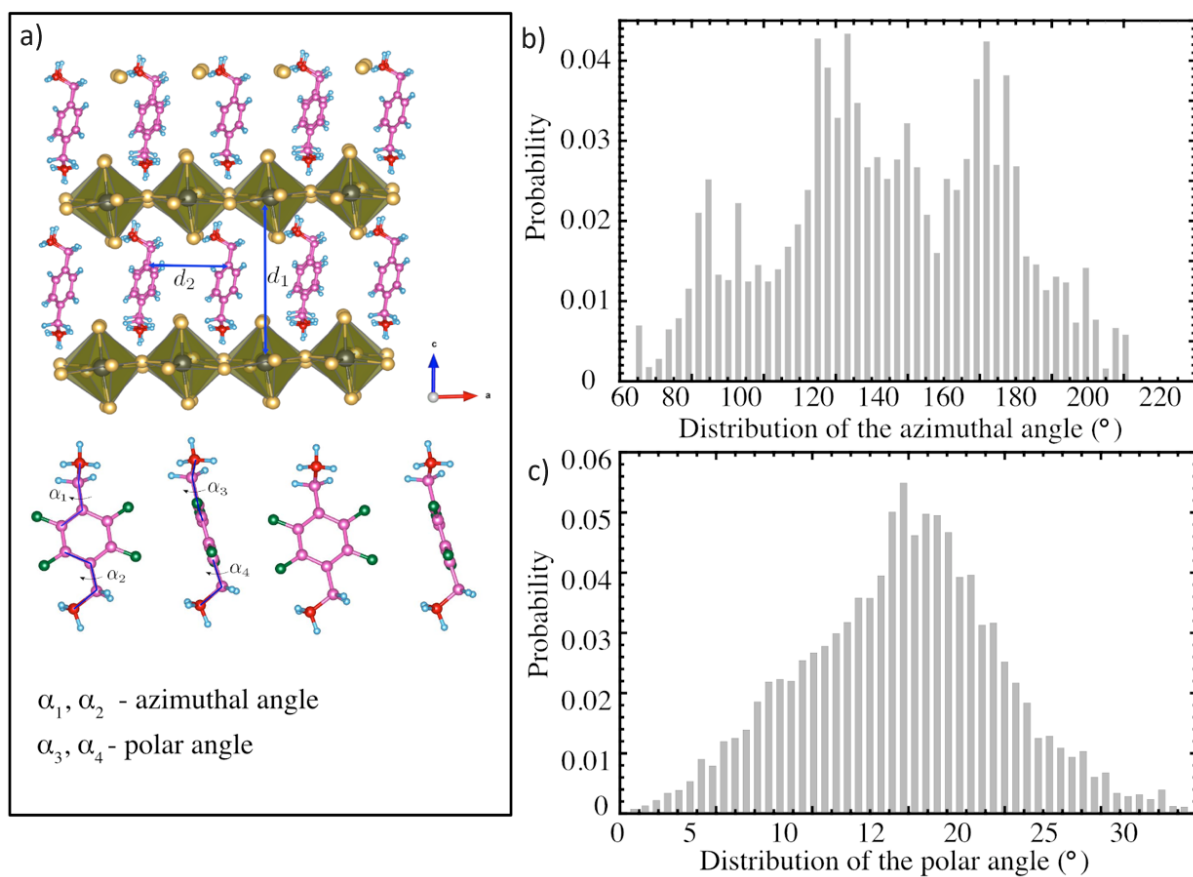
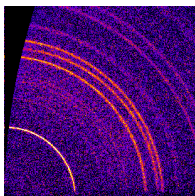


Figure D.33: (a) DFT (PBEsol)-optimized structure of (PDMA)PbI₄ with the definition of structural parameters: d_1 , d_2 and $\alpha_1 - \alpha_4$. (b) – (c) Distribution of polar (θ) and azimuthal (ϕ) angles for (PDMA)PbI₄: θ refers to inclination of spacers with respect to the c -axis, and ϕ indicates their in-plane rotation in the a,b -plane. Image taken from publication [IV].

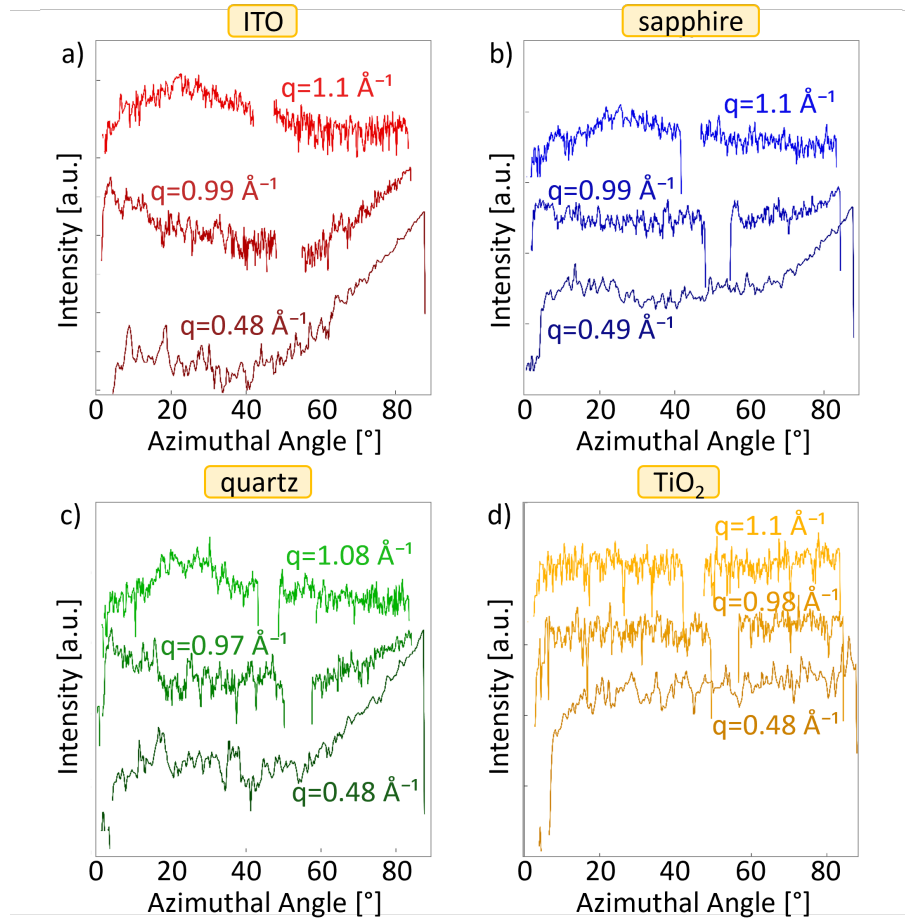
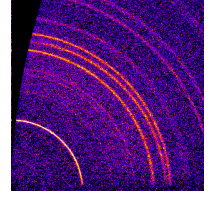


Figure D.34: Angular intensity profiles of the ring-shaped diffraction signals in the reciprocal space maps in Figure 11.7 (a)–(d) corresponding to (PDMA)PbI₄ thin films on different substrates. (a) ITO, (b) sapphire, (c) quartz, (d) *m*-TiO₂.

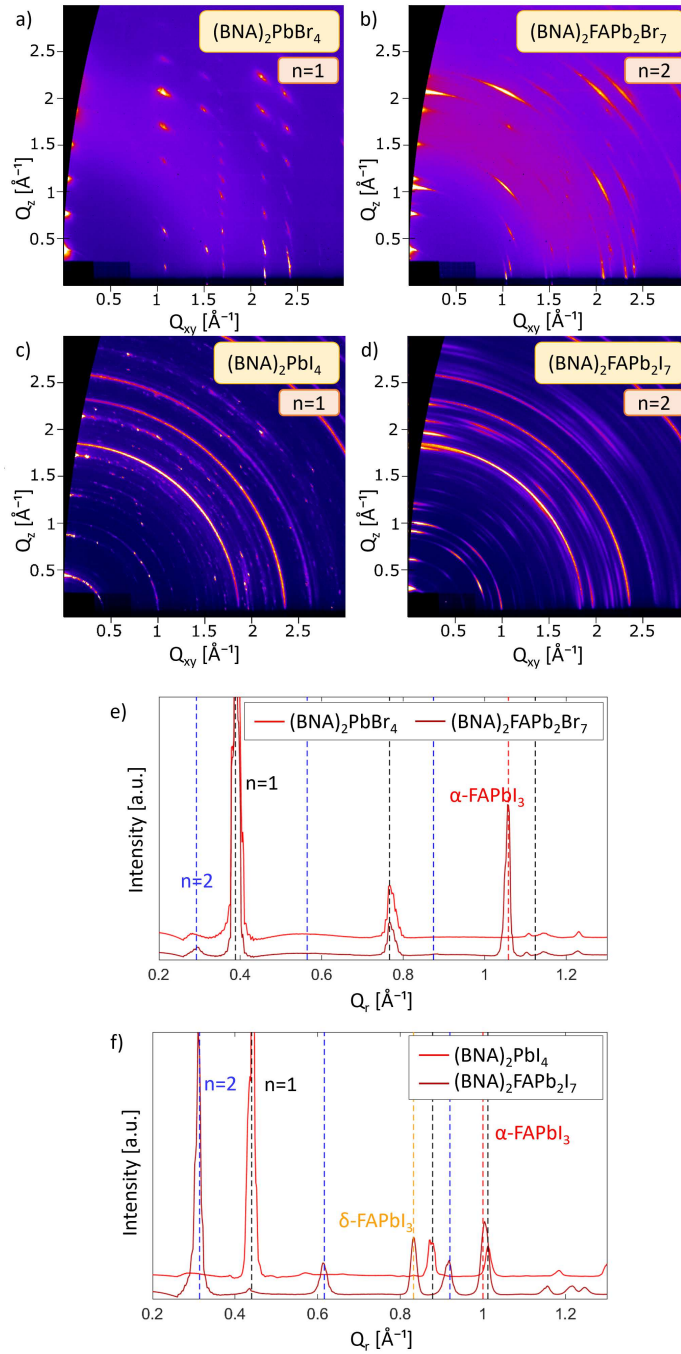
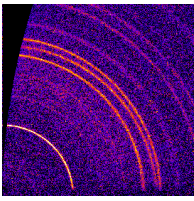


Figure D.35: GIWAXS reciprocal space maps of layered benzylammonium-based samples with $(\text{BNA})_2\text{FA}_{n-1}\text{Pb}_n\text{X}_{3n+1}$ composition (a) $\text{X}=\text{Br}$ $\tilde{n}=1$, (b) $\text{X}=\text{Br}$ $\tilde{n}=2$, (c) $\text{X}=\text{I}$ $\tilde{n}=1$, (d) $\text{X}=\text{I}$ $\tilde{n}=2$. (e) Radial profiles of reciprocal space maps in (a) and (b) for bromide-based samples. (f) Radial profiles of reciprocal space maps in (c) and (d) for iodide based samples. Vertical dashed lines in (e) and (f) indicate different crystal phases: black: $n=1$ phase, blue: $n=2$ phase, red: $\alpha\text{-FAPbI}_3$, yellow: $\delta\text{-FAPbI}_3$. A much higher degree of orientational order can be observed for the bromide-based samples as well as an increased presence of the $n=1$ phase in $\tilde{n}=2$ samples.

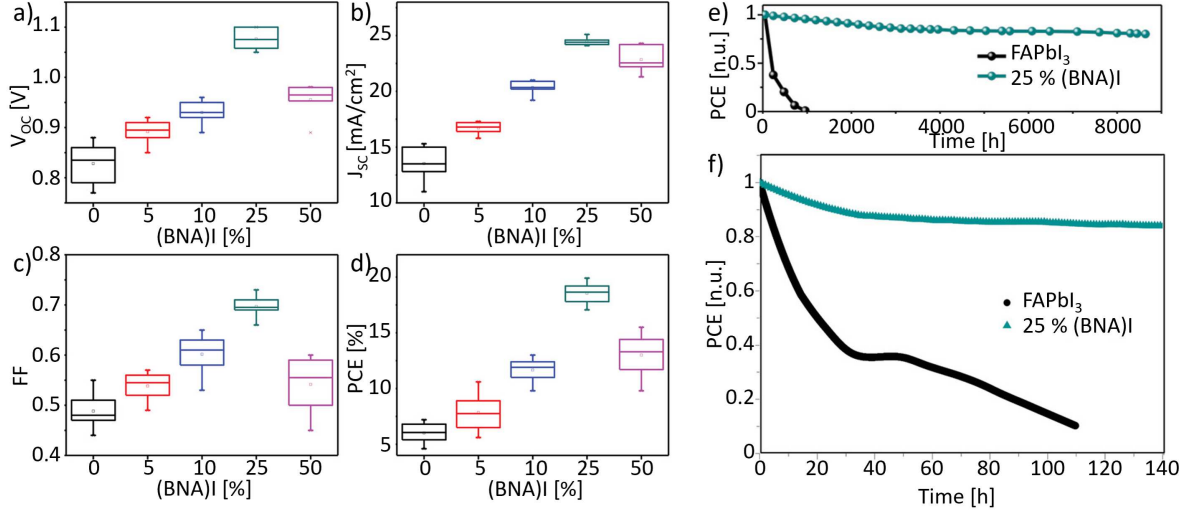
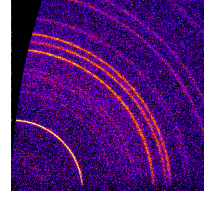


Figure D.36: Photovoltaic parameters for 20 devices based on $FAPbI_3(BNAI)_x$ ($x = 0, 0.05, 0.10, 0.25$, and 0.50) compositions. (a) open circuit voltage (V_{OC}), (b) short circuit current (J_{SC}), (c) fill factor (FF), (d) power conversion efficiency (PCE). (e) Average shelf stability by monitoring the evolution of performance of the corresponding non-encapsulated solar cells exposed to the ambient environment with relative 40 % humidity in the dark at ambient temperature (n.u. = normalized units with respect to the initial performance). Initial $PCE = 20\%$. (f) Normalized PCE of neat $FAPbI_3$ and $FAPbI_3(BNAI)_{0.25}$ based devices monitored under continuous white light exposure in nitrogen atmosphere, at $25^\circ C$, as a function of time (140 h). Initial $PCE = 19\%$. Image modified from publication [VI].

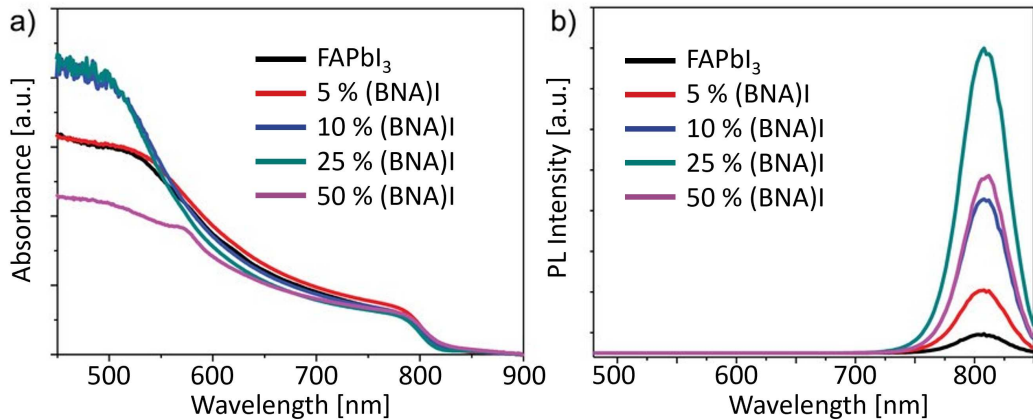


Figure D.37: Optical characterization of the $FAPbI_3(BNAI)_x$ perovskite films of various compositions x . (a) UV-vis absorption, (b) photoluminescence spectroscopy. Image modified from publication [VI].

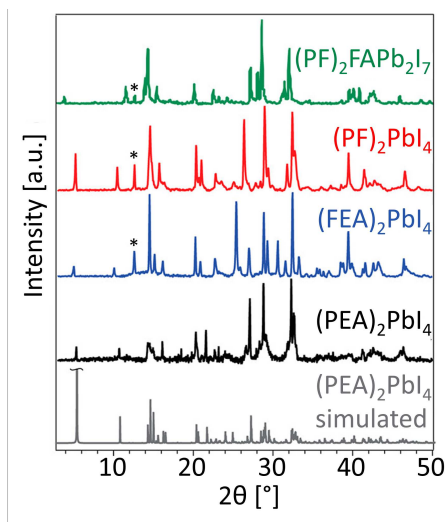
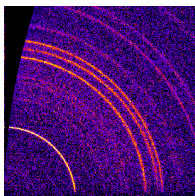


Figure D.38: PXRD patterns of mechanosynthesized layered hybrid perovskites of $S_2FA_{n-1}Pb_nI_4$ composition ($S = \text{PEA}$, FEA and 1:1 $\text{PEA}:\text{FEA}$ denoted PF). The simulated pattern for $(\text{PEA})_2\text{PbI}_4$ is shown for the previously reported (twisted) crystal structure.⁴⁸ The major PbI_2 reflection is marked with an asterisk. Image taken from publication [VII].

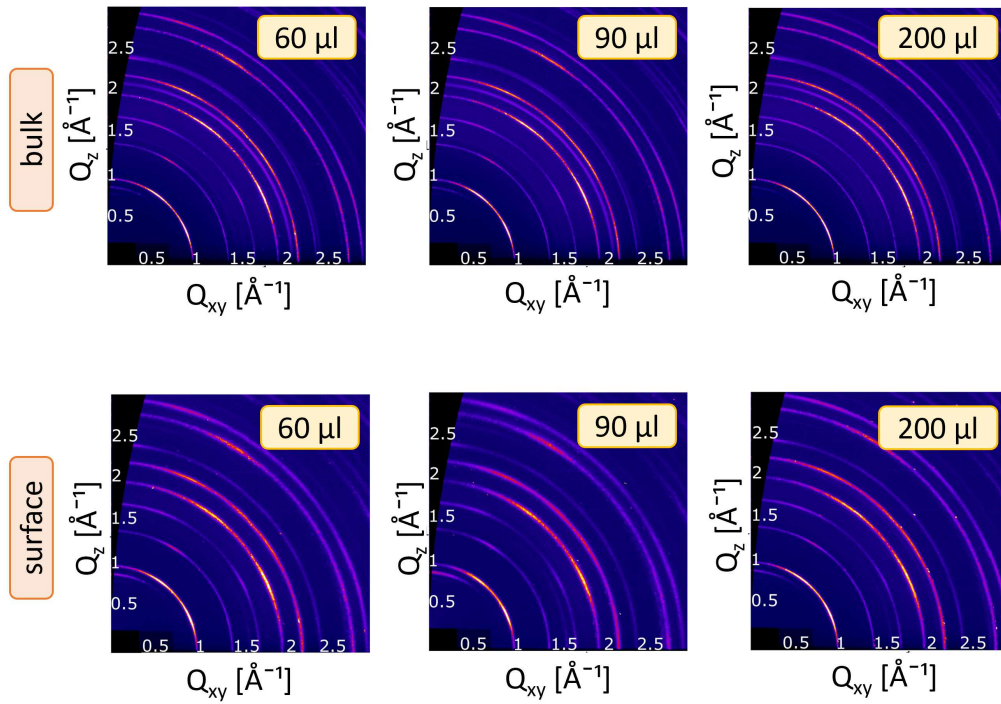
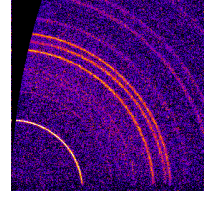


Figure D.39: GIWAXS reciprocal space maps of triple-cation $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ perovskite thin film samples obtained by pipetting different volumes of trifluorotoluene antisolvent. Bottom row: probing the film surface (incidence angle of 0.1°); top row: probing the bulk material (incidence angle of 0.3°). Image modified from publication [VIII].

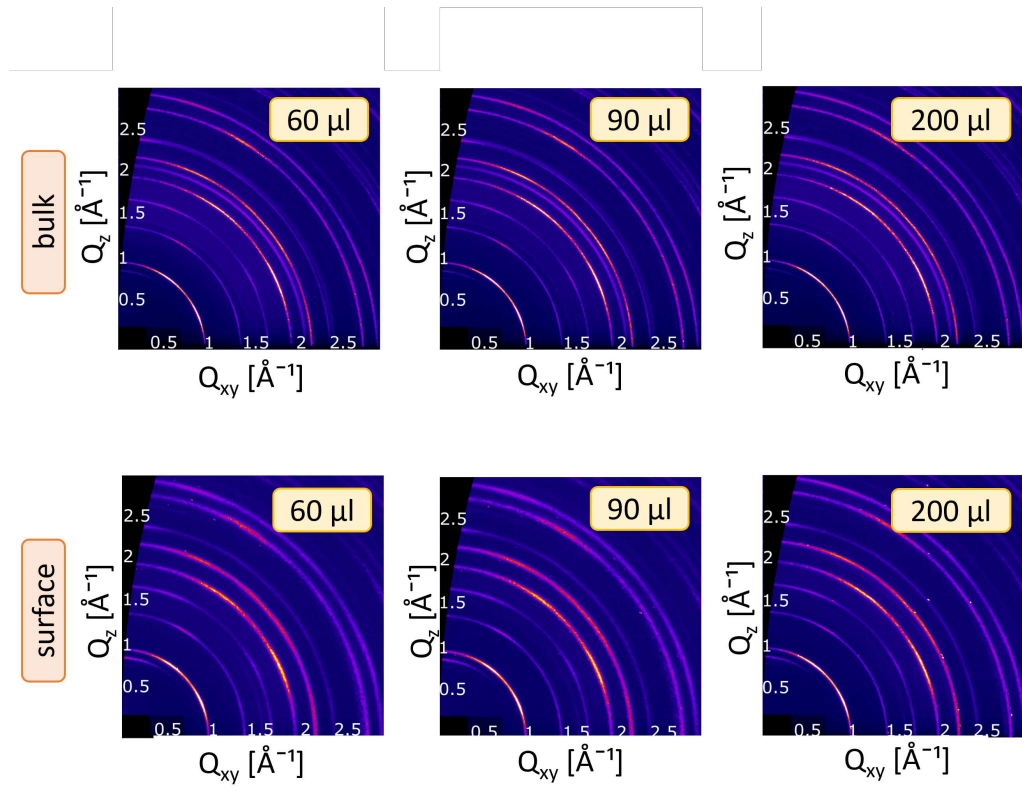
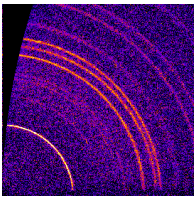


Figure D.40: GIWAXS reciprocal space maps of triple-cation $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ perovskite thin film samples obtained by spraying different volumes of trifluorotoluene antisolvent. Bottom row: probing the film surface (incidence angle of 0.1°); top row: probing the bulk material (incidence angle of 0.3°). Image modified from publication [VIII].

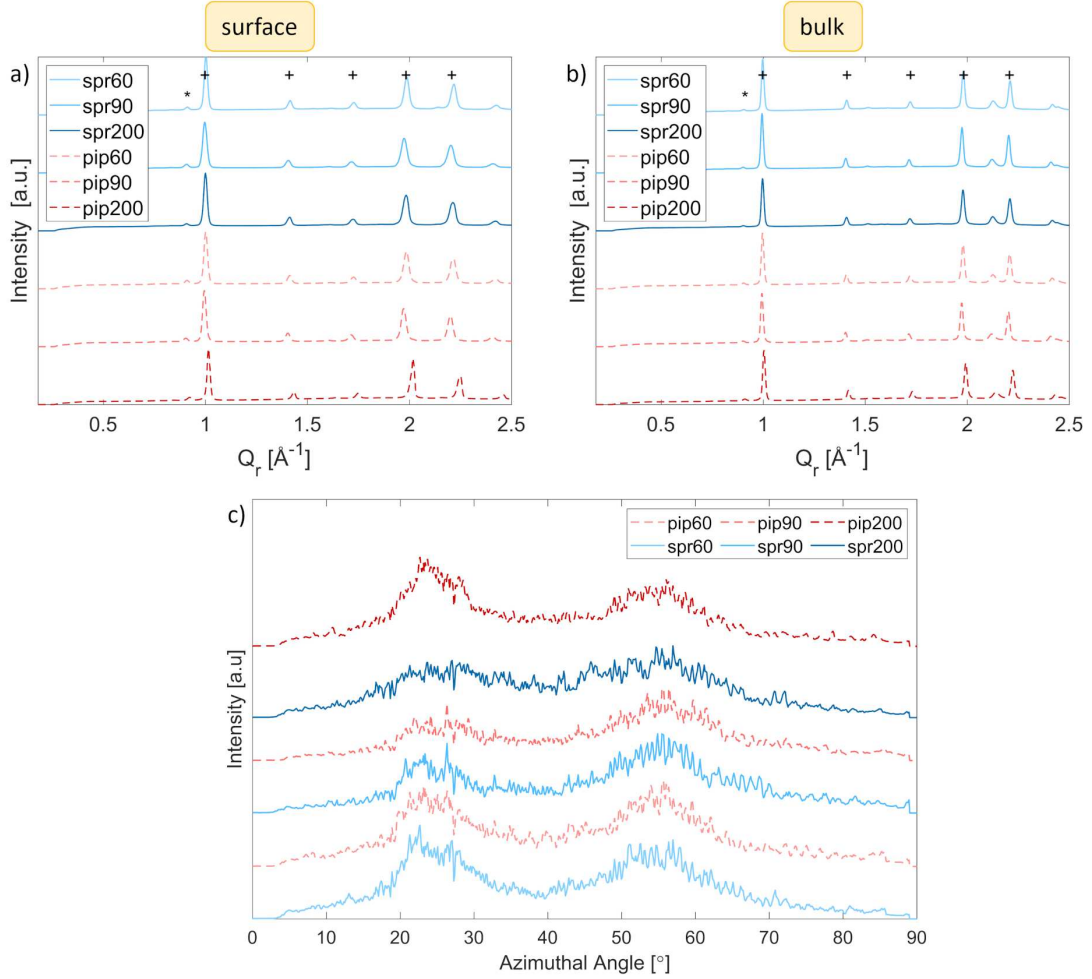
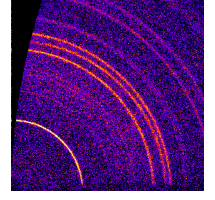


Figure D.41: Radial profiles of reciprocal space maps in Figures D.39 and D.40. (a) probing the film surface (incidence angle of 0.1°); (b) probing the bulk of the film (incidence angle of 0.3°). (c) Azimuthal angular profiles of the (100) perovskite diffraction ring in the reciprocal space maps in Figures D.39 and D.40, top row, indicating preferred orientation of the perovskite crystallites. Image taken from publication [VIII].

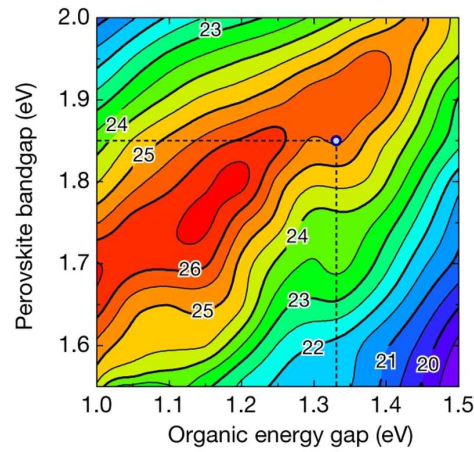
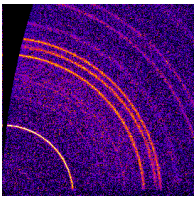


Figure D.42: Semi-empirical model of the tandem cell efficiency versus the energy gap of organic and perovskite subcells. The intersection of the dashed lines corresponds to the energy gap of the PM6:Y6:PC₆₁BM back-cell and the matching energy gap of the perovskite front-cell. This simulation states a conservative scenario assuming open-circuit voltage loss (ΔV_{OC}) of 0.5 V and a fill factor of 80 %.

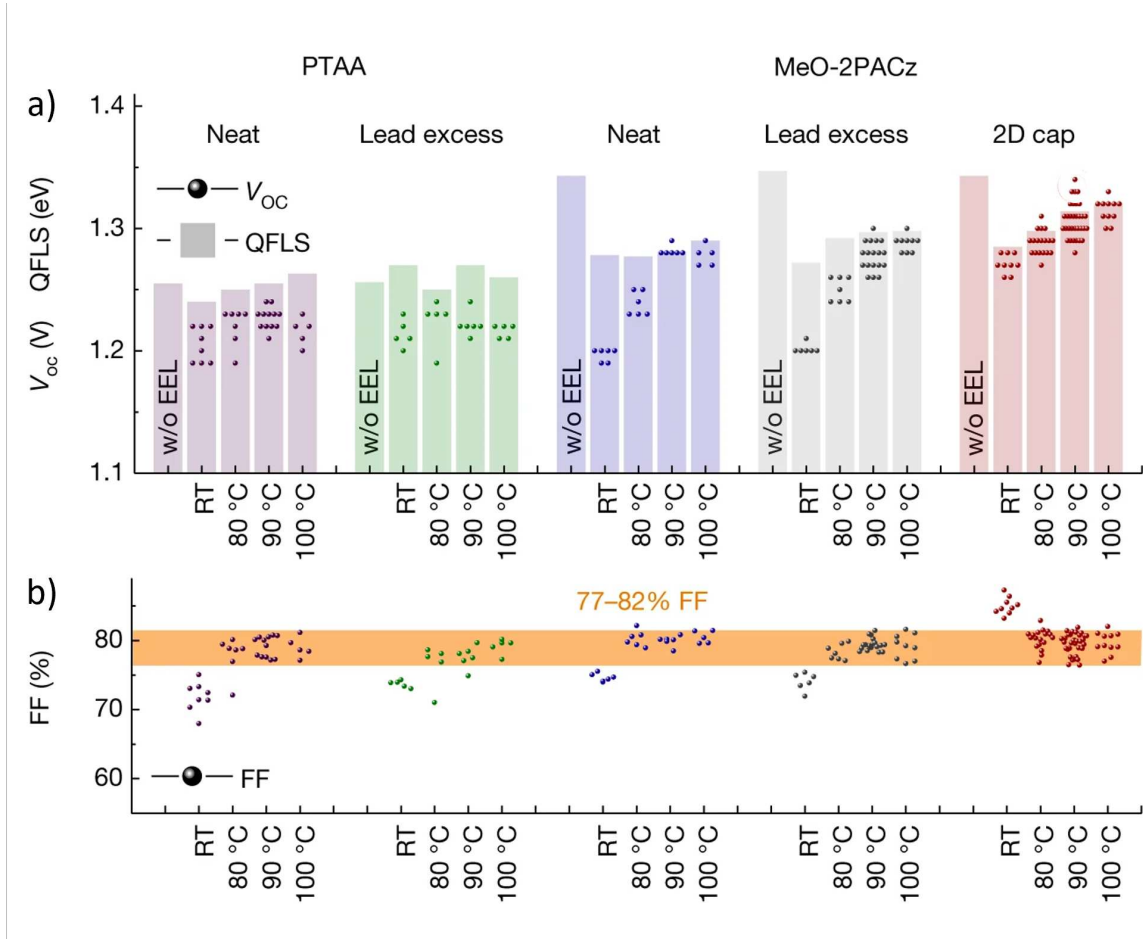
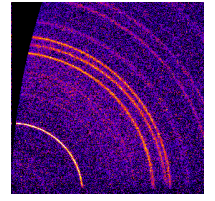


Figure D.43: (a) Comparison of the open-circuit voltage (V_{OC}) of actual perovskite solar cells with the corresponding quasi-Fermi level splitting of representative layer stacks with and without electron extraction layers and varied device-annealing temperature (room temperature). The fill factor (FF) of each cell type is shown in (b). The different temperatures refer to the annealing conditions after deposition of the aluminum zinc oxide nanoparticle layer. The dots represent the results of individual devices and indicate the experimental spread.

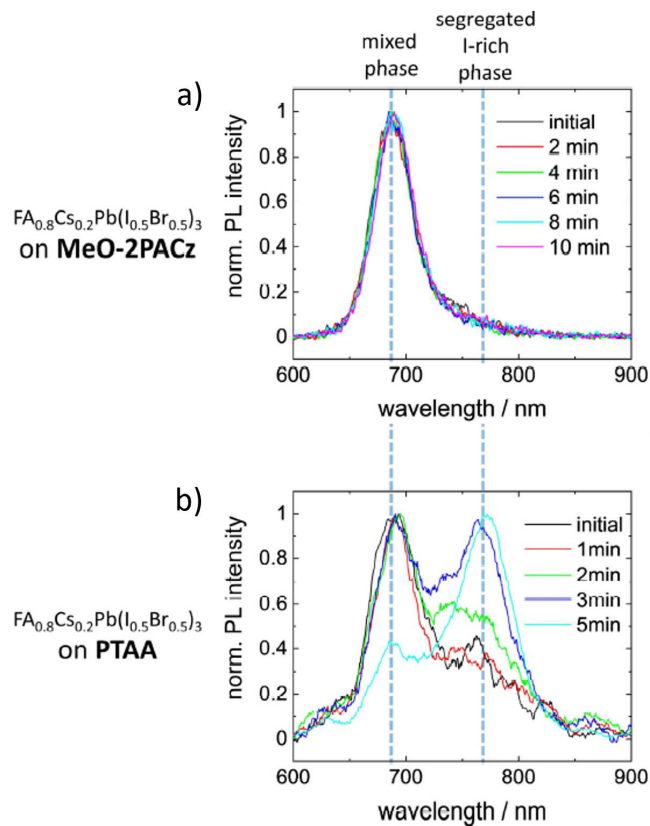
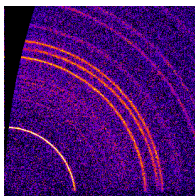


Figure D.44: Development of photoluminescence of $\text{FA}_{0.8}\text{Cs}_{0.2}\text{Pb}(\text{I}_{0.5}\text{Br}_{0.5})_3$ on top of (a) MeO-2PACz and (b) PTAA. The dashed lines indicate the photoluminescence maxima of the mixed and the segregated, iodide rich phase. Excitation was performed with one sun equivalent.

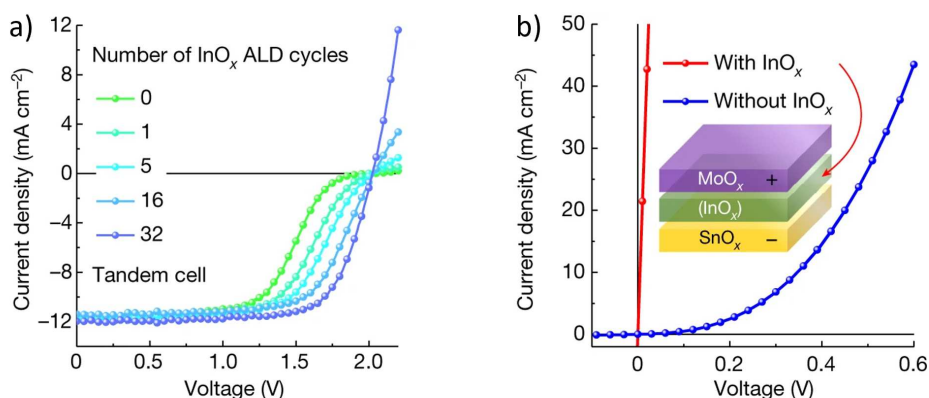
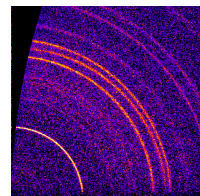


Figure D.45: (a) J-V characteristics of tandem cells with varied thickness (number of atomic layer deposition (ALD) cycles) of the InO_x interconnect. (b) J-V characteristics of $\text{SnO}_x/(\text{InO}_x)/\text{MoO}_x$ diodes.



Appendix E

Acknowledgements

This thesis would not be complete without acknowledging the support of many people who contributed to this work either scientifically or in many other ways.

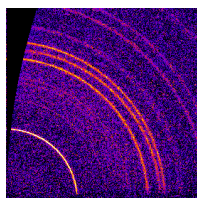
First of all, my sincere thanks are due to Prof. Frank Schreiber for providing me the opportunity to conduct my PhD studies in his group. I am grateful for his trust in my abilities and the support he has shown me throughout the years.

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Of course, I cannot name every member of the group here, but I want to thank everyone

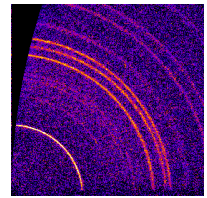


who made these last five years a pleasant experience by creating a friendly work environment in Tübingen as well as on many trips to conferences, beamtimes and the annual group retreats.

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APPENDIX E. ACKNOWLEDGEMENTS
