
Ultrafast Spectroscopy of Charge-Carrier Dynamics and Stability in Lead-Halide Perovskites for Thin-Film Photovoltaics



Waqas Rehman

Pembroke College
University of Oxford

A thesis submitted for the degree of
Doctor of Philosophy

Trinity 2017

Abstract

Ultrafast Spectroscopy of Charge-Carrier Dynamics and Stability of Lead-Halide Perovskites for Thin-Film Photovoltaics

Waqas Rehman, Pembroke College

Submitted for the degree of Doctor of Philosophy in Trinity Term 2017

Hybrid metal halide perovskites have emerged as an important new class of materials for photovoltaics. For their integration in tandem solar cells, optimised photocurrent matching between top and bottom cells requires careful control over bandgap energy and charge transport properties, for which tunable mixed bromide-iodide lead perovskites are the most prominent contenders. This thesis investigates photophysical properties of highly tunable mixed-halide and mixed-cation perovskite films with the aim of correlating their optoelectronic parameters with crystal phase changes induced by compositional variations.

Firstly, the compositional variation of mixed-halide $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites is explored. Bimolecular and Auger charge-carrier recombination rate constants strongly correlate with the bromide content, x , suggesting a link with electronic structure. With rising x , the constants increase by up to an order of magnitude, yet still remain significantly below the Langevin limit. FAPbBr_3 and FAPbI_3 exhibit charge-carrier mobilities of 14 and 27 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and diffusion lengths exceeding 1 μm , while mobilities across the mixed bromide-iodide system depend on crystalline phase disorder. Particularly, the mid-bandgap and bromide rich regions are found to be disordered and prone to photo-induced halide segregation.

Subsequently, a highly crystalline mid-bandgap mixed-cation lead mixed-halide $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite is developed and investigated with focus on understanding the impact of adding caesium to the A-cation site in the lattice. Compared to single-cation $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$, the crystal phase is stable and the charge-carrier mobility measured from THz spectroscopy reaches 21 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ resulting in a diffusion length of 3 μm . With photoinduced halide segregation being inherently suppressed, another benefit of controlled A-cation mixing could be revealed.

In an aging-study, the correlation between the colloids concentration present in the precursor solution of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ and nucleation stages for the crystallization of perovskite is explored. Having direct impact on morphology and photophysical properties, charge-carrier mobilities are reported to correlate with colloid concentration reaching $> 20 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for an optimum concentration.

Ultimately, the full parameter space of mixed-cation ($0 < y < 1$) lead mixed-halide ($0 < x < 1$) $\text{Cs}_y\text{FA}_{1-y}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites is examined, where crucial links between crystal phase stability, photo-stability and optoelectronic properties are highlighted. Finely tuning the caesium cation in the lattice yields excellent structural stability and charge-carrier transport properties for the parameter space between $0.1 < y < 0.3$. For an optimized caesium content, the orthogonal halide-variation parameter space for $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ achieves charge-carrier mobilities of 11 – 40 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and diffusion lengths of 0.8 – 4.4 μm .

List of Publications

Manuscripts Published in Peer-Reviewed Journals

- **W. Rehman**, R. L. Milot, G. E. Eperon, C. Wehrenfennig, J. L. Boland, H. J. Snaith, M. B. Johnston and L. M. Herz. Charge-Carrier Dynamics and Mobilities in Formamidinium Lead Mixed-Halide Perovskites. *Adv. Mater.*, **2015**, 27, 7938-7944.
- D. P. McMeekin, G. Sadoughi, **W. Rehman**, G. E. Eperon, M. Saliba, M. T. Horantner, A. Haghighirad, N. Sakai, L. Korte, B. Rech, M. B. Johnston, L. M. Herz and H. J. Snaith. A Mixed-Cation Lead Mixed-Halide Perovskite Absorber for Tandem Solar Cells. *Science*, **2016**, 351, 151-155.
- **W. Rehman**, D. McMeekin, J. Patel, R. Milot, M. B. Johnston, H. Snaith and L. M. Herz. Photovoltaic mixed-cation lead mixed-halide perovskites: Links between crystallinity, photo-stability and electronic properties. *Energy Environ. Sci.*, **2016**, 10, 361-369.
- D. P. McMeekin, Z. Wang, **W. Rehman**, F. Pulvirenti, J. B. Patel, N. K. Noel, S. R. Marder, M. B. Johnston, L. M. Herz and H. J. Snaith. Crystallization Kinetics and Morphology Control of Formamidinium-Cesium Mixed-Cation Lead Mixed-Halide Perovskite via Tunability of the Colloidal Precursor Solution. *Adv. Mater.*, **2017**, 29, 1607039.

Acknowledgements

Firstly, I would like to express the greatest of appreciation for my supervisor Prof Laura Herz, who committed a lot of her time and effort to provide me with excellent advice and feedback regarding my results and the overall progress of my work. Particularly, I benefited a great deal from her specialist knowledge and thought leadership which have had a great share in making this work possible. I am also very grateful for the help provided by Prof Michael Johnston, especially for valuable advice regarding technical aspects of my work.

Moreover, I consider myself fortunate for having been surrounded by competent colleagues, who helped with making this work not only possible but also an enjoyable experience. Special thanks to Christian Wehrenfennig, Patrick Parkinson and Rebecca Milot for teaching me the many practical pointers and techniques required to understand and conduct terahertz experiments. I would also like to thank everyone in my research group, especially Jessica Boland, Juliane Gong, Adam Wright, Jay Patel and many others for getting me introduced to all kinds of laboratory equipments as well as for always being up for a friendly piece of advice. The atmosphere in the group has always been truly cordial on all levels of interaction. Furthermore, this work largely relied on a strong collaboration with Prof Henry Snaith whom I would like to thank for the opportunity to study first-hand state-of-the-art photovoltaic materials. I feel obliged to many members of his research group, especially Giles Eperon and David McMeekin, for fruitful discussions and providing me with high-quality samples.

At this point, I would also like to express how grateful I am to my family, especially to my parents for supporting me in every situation. Finally, a lot of credit goes to my wife Amina for being very supportive and a wonderful companion even during the most demanding times in this period.

Contents

1	Introduction	1
2	Literature Review	5
2.1	Perovskite Crystal structure	5
2.2	Perovskite Solar Cells	8
2.2.1	Discovery and Rise	8
2.2.2	Deposition Techniques and Device Architectures	9
2.2.3	Optimisation via Compositional and Interfacial Engineering	12
2.3	Perovskite Tandem Solar Cells	14
2.4	Scale-Up Technologies for Perovskites	16
2.5	Stability of Perovskites	17
2.5.1	Structural Stability	17
2.5.2	Ambient Air Oxygen	20
2.5.3	Ambient Air Moisture	21
2.5.4	Photo-Induced De-Mixing in Mixed-Halide Perovskites	22
2.6	Optoelectronic Properties	26
2.6.1	Electronic Structure of Perovskites	26
2.6.2	Charge-Carrier Transport Properties	27
3	Experimental Techniques	32
3.1	THz Spectroscopy	33
3.1.1	Optical Pump - Terahertz Probe Spectroscopy	34

3.1.2	THz Generation	35
3.1.3	THz Detection: Electro-Optic Sampling	36
3.1.4	Optical-Pump THz-Probe Experimental Setup	37
3.1.5	Data Analysis	41
3.2	Photoluminescence Spectroscopy	45
3.2.1	Steady-State Photoluminescence	45
3.2.2	Time-Correlated Single Photon Counting	46
3.2.3	Time-dependent Photoluminescence Stability	51
3.2.4	Data Analysis	51
4	Charge-Carrier Dynamics and Stability of Formamidinium Lead Mixed-Halide Perovskites	54
4.1	Sample Preparation	56
4.1.1	Perovskite Precursor Synthesis	56
4.1.2	Film Fabrication	56
4.2	Results and Discussion	57
4.2.1	Structural and Optical Characterisation	57
4.2.2	Electronic Characterisation	63
4.2.3	Conclusions	74
5	Charge-Carrier Dynamics and Stability of Mixed-Cation Lead Mixed-Halide Perovskites	76
5.1	Sample Preparation	78
5.1.1	Perovskite Precursor Synthesis	78
5.1.2	Perovskite Precursor Solution Mixture	78
5.2	Results and Discussion	79
5.2.1	Structural and Optical Characterisation	79
5.2.2	Electronic Characterisation	86

5.2.3	Photovoltaic Device Performance	91
5.2.4	Crystallization Kinetics and Charge-Carrier Transport	93
5.2.5	Conclusions	99
6	Mixed-Cation Lead Mixed-Halide Perovskites: Links between Crystallinity, Photo-Stability and Electronic Properties	101
6.1	Sample Preparation	102
6.1.1	Perovskite Precursor Solution Mixture	102
6.1.2	Film Fabrication	103
6.2	Results and Discussion	103
6.2.1	Optoelectronics and Stability of $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$	103
6.2.2	Optoelectronics of $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$	123
6.2.3	Conclusion	135
7	Conclusion and Outlook	137

Chapter 1

Introduction

Owing to the steady growth of human populations pushing for economic growth and higher standards of living, world power consumption is at its peak and showing no signs of stagnation. Conventional energy sources, such as fossil fuels, traditionally have dominated the energy and utilities landscape. In recent years, their continuous depletion and a growing awareness around their environmentally harmful nature has increasingly put them on the retreat, thereby making way for non-exhaustive, renewable energy technologies [1]. Renewable sources based on photovoltaic technology draw on the immense availability of solar energy from the sun that can be converted into electrical energy via the photovoltaic effect. As of early 2017, the cumulative capacity of installed solar modules exceeds 350 GW with grid parity achieved in dozens of countries across the world [2]. Nevertheless, the photovoltaic sector needs to overcome further obstacles if it wants to become the most cost-efficient source of power generation. One way to solve this is by increasing efforts to mitigate solar power fluctuations via improving existing energy storage technologies. Another more imminent approach promotes further cost-reductions by finding cheaper alternatives to existing photovoltaic materials, such as the currently dominating crystalline silicon. This is particularly challenging since silicon modules have already seen a drastic cut in prices as a result of overcapacities in production and technological advancements [3]. However, since the turn of the millennium, scientific progress on thin-film fabrication

techniques and novel materials have prompted the development of ‘next-generation’ photovoltaic technologies with the attempt to match or supersede crystalline silicon solar cells in terms of costs, efficiencies and long-term stability. Amongst them, organic photovoltaics (OPV) employing organic constituents for light harvesting or charge-carrier transport and mesoscopic solar cells, in particular dye-sensitized solar cells (DSSC), have been dealt with extensively as potential contenders [4, 5]. However, because of their charge-carrier lifetimes and power conversion efficiencies being significantly lower than conventional multi-crystalline silicon or CdTe cells, to this day, their scope of application has been fundamentally limited, especially regarding large-scale modular application in power solar plants.

A newly emerging candidate to overcome these shortfalls is represented by solid-state organic-inorganic solar cells that form the perovskite crystal structure ABX_3 . This class of materials has seen a phenomenal rise reaching certified efficiencies of up to 22.1% within just a few years (Figure 1.1) [6, 7]. Early investigations of tri-halide $CH_3NH_3PbI_3$ (MAPbI₃) or $CH_3(NH_2)_2PbI_3$ (FAPbI₃) perovskites reveal broad absorption of light in the visible range [8] and encouraging optoelectronic properties [9]. As for OPVs and DSSCs, another crucial benefit of such perovskite materials is that their bandgap can be tuned relatively easily and widely with chemical composition, that is via mixing X-site halides, for example bromide and iodide. This allows for attractive coloration and tandem solar cell designs. Also, mixing A-site cations is reported to have strongly beneficial effects on structural stability and power conversion efficiencies [10]. However, given the importance of this heterogeneous material system, the dynamics of photoexcited charge-carriers and their mobilities as a function of mixed-halide bromide-iodide or mixed-cation formamidinium-methylammonium-caesium content are not sufficiently well understood. Yet, a detailed knowledge of these properties is essential for significantly improving photovoltaic devices that employ these highly tunable materials. The work presented in this thesis reports on a

three-part series of experimental studies conducted to determine key optoelectronic properties in mixed-cation lead mixed-halide perovskite films for the purpose of assessing their potential as future absorber layers in highly efficient solar cell devices.

Chapter 2 provides an overview of wide-ranging topics of the broader hybrid perovskite research area. The multi-faceted properties of hybrid perovskites including their rapid evolution as solar cell absorbers are discussed, closing with detailed accounts on the state-of-the-art regarding stability aspects and optoelectronic properties.

Chapter 3 presents an overview of the experimental setups used in this work. These are mainly based on different (time-resolved) spectroscopic techniques relying on ultrafast optical excitation and terahertz radiation enabling insights into the response of mobile charge-carriers and their sub-picosecond dynamics.

In **Chapter 4**, the $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ lead mixed-halide perovskite series is explored for bandgap tunability, photoluminescence stability and charge-carrier transport as a function of varying halide fractions across the entire bromide-iodide range.

Chapter 5 describes findings obtained for adding caesium to the A-site cation in the mid-bandgap, amorphous $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite. The study has a particular focus on addressing the impact of crystal phase stabilisation via A-site cation mixing on photoluminescence-stability and optoelectronic parameters, such as charge-carrier dynamics and mobilities.

Chapter 6 presents an extensive follow-up work analysing the entire orthogonal parameter space of mixed-cation lead mixed-halide perovskites, first varying A-site cations in $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$, and then X-site halides in $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ films, for the principal purpose of finding regions of enhanced crystallinity and reflections thereof in optoelectronic properties, while also comparing them to the single-cation equivalents discussed in Chapter 4.

Finally, **Chapter 7** summarizes and contextualises chief outcomes of the work presented in this thesis, and gives an outlook of possible investigations in the future.

Chapter 2

Literature Review

2.1 Perovskite Crystal structure

The term perovskite originates from the structure of the mineral CaTiO_3 , discovered by Russian mineralogist Lev Aleksevich von Perovski in the 19th century. It adopts a crystal structure that follows the general stoichiometry of ABX_3 and has become the name giver for all compounds forming this particular crystal structure [11]. The structure consists of A-site cations at the corners of the cube (Figure 2.1), a body-centered divalent B-site cation and X-site metal anions in face-centered positions [12]. From the perspective of the B-cations, the structure can be described as a three dimensional net of corner-sharing $[\text{BX}_6]$ octahedra formed by the X-site metal anions with the A-cations occupying the gaps in between the octahedral cages (Figure 2.2). In most organo-metal-halide perovskite (OMHP) semiconductors, A is a an organic cation (e.g. Formamidinium (FA^+) or Methylammonium (MA^+)), B, a divalent metal cation (e.g. Pb^{2+} or Sn^{2+}), and X_3 can be composed of one or more types of halide anions (e.g. iodide (I^-), bromide (Br^-) or chloride (Cl^-)) [13]. Ideally, any given OMHP crystallises in the cubic phase which carries the highest crystal symmetry corresponding to the space group Pm-3m [12]. It consists of rigid spheres, where each cation in the lattice is of the perfect size to maintain stable contact with an anion. Through ion size variations, the cubic lattice can undergo distortion via octahedral tilting that

causes an alteration of the lattice parameters. For example, with a decreasing size of A-site cations, it comes to a point where the cations are unable to maintain the contact with the anions and at the same time preserve the cubic structure. Generally, this is attributed to a slight bending of the B-X-B metal-halide bond, tilting the BX_6 octahedra to bring the anions into contact with A-site cations [14]. The resulting lower-symmetry variations of the crystal lattice (e.g. tetragonal, trigonal, or orthorhombic phases) have direct implications on the stability in a wide range of perovskite materials [15]. Upper and lower boundaries for measuring the stability of perovskite crystals are expressed by the *Goldschmidt tolerance factor* t . It effectively correlates the different ionic radii existing in the perovskite [16]. Considering the cubic lattice as the ideal base, the tolerance factor aims to provide an estimate for the extent of distortion and thus presents a measure for assessing the structural stability in the crystal:

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

where R_A , R_B and R_X describe the relative ionic radii of the respective A-, B-, and, X-site components in the perovskite. For example, a tolerance factor of $0.8 < t < 1.0$ corresponds to the desired cubic crystal structure at finite temperature, while a departure from this interval towards either end, could result in the emergence of orthorhombic ($t < 0.8$) or hexagonal crystal phases ($t > 1.0$) (Figure 2.3) at the expense of a more symmetric cubic lattice structure [17].

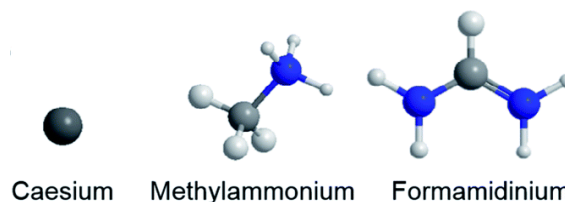


Figure 2.1: A-site cations used in photovoltaic APbX_3 perovskites. Taken from [18].

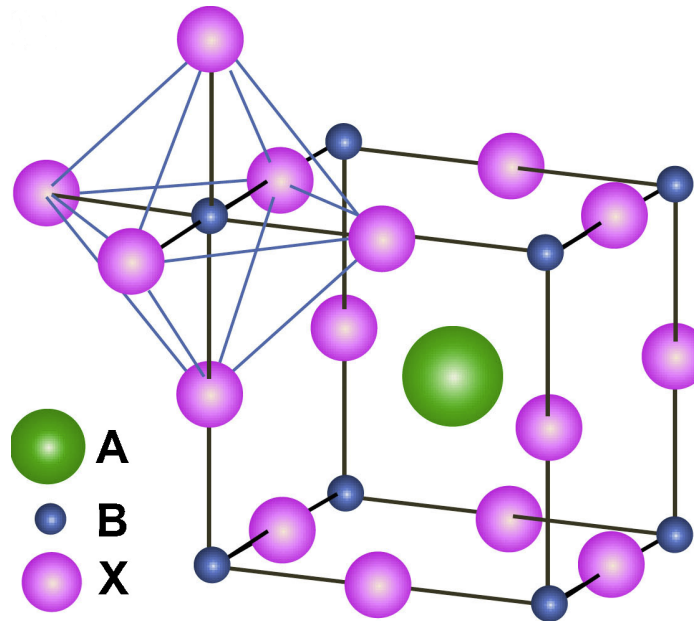


Figure 2.2: Sketch of an ideal cubic perovskite crystal structure with the A-site cation (green), B-site metal anion (blue), and X-site halide anion (magenta). The latter two components form a $[BX_6]$ octahedral cage. Taken from [19].

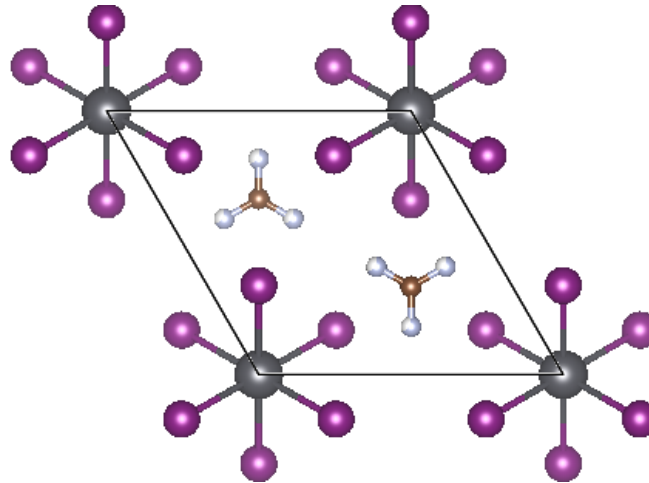


Figure 2.3: Unit cell structure of the hexagonal non-perovskite δ -phase of $FAPbI_3$.

2.2 Perovskite Solar Cells

2.2.1 Discovery and Rise

Today, a large variety of hybrid materials adopting the perovskite crystal structure are known and well understood. In the 1990s, a concurrent but separate research effort by Japanese groups and Mitzi and co-workers led to the extensive study of optical and physical properties in layered hybrid perovskites, providing insights into antiferromagnetism, piezoelectricity, thermoelectricity, conductivity, superconductivity, - and in the present context most notably - semiconducting properties [20] - [22]. The studied materials were also sometimes reported to show excitonic features and a reasonable mode of operation in optoelectronic devices such as LEDs and transistors [23] - [27].

However, the time for OMHPs to be used as active absorbers in solar cells was not ripe, until in 2009, it occurred to Kojima et al. that employing methylammonium lead halide perovskite nanocrystals as a sensitizer in mesoporous metal-oxide (TiO_2) liquid-electrolyte sensitised solar cells could be a promising replacement for rather costly and difficult-to-synthesize molecular dyes [28]. Photovoltaic devices based on this approach, reached low but encouraging power conversion efficiencies (PCE) of 3.8%. This was aided by the perovskite's ability to strongly absorb light over a broad spectrum in the visible range, to an extent that reducing film thickness significantly presented a realistic opportunity for further optimisation. This groundbreaking development suggested a compelling suitability of perovskite semiconductors as future light-harvesting materials and triggered a wave of further research efforts across the globe. Two years on, optimising the TiO_2 metal-oxide surface and processing the perovskites as quantum-dots further ramped up the PCE to 6.5% [29].

2.2.2 Deposition Techniques and Device Architectures

However, owing to the perovskites' propensity towards quickly decomposing and degrading in the liquid electrolyte, research soon moved towards more stable all-solid-state devices based on a range of different architectures incorporating hybrid interfaces. In 2012, one concept emulated solid-state dye-sensitised solar cells, using the perovskite material as an absorber infiltrated into an electron-extracting mesoporous TiO_2 metal-oxide layer [30]. Concurrently, another research group developed a meso-superstructured solar cell (MSSC) configuration incorporating an insulating low-temperature-processed mesoporous Al_2O_3 scaffold for film-formation assistance, leaving the commonly used TiO_2 aside. In this way a faster electron transfer to the anode also helped in overcoming the voltage drop otherwise associated with electron transfer to TiO_2 [31, 32]. Besides, both devices equally employed a solid-state hole transporting material (spiro-OMETaD). The resulting PCEs crossed the landmark of 10%, respectively.

The p-i-n junction in a MSSC device is formed by a hole-extracting layer, the perovskite, and a thin electron-extracting layer and can be considered an evolution of a sensitised solar cell that allows for lower processing temperatures and better cell stability. Nonetheless, the noticeably self-sufficient absorption and charge transport ability of OMHPs hint at the potential for discarding more device complexity than needed for MSSC device fabrication. It may further be assumed that if employing a mesoporous Al_2O_3 scaffold only assists the film-formation process, its use could be superseded by simply improving film processing conditions [33]. For example, in a planar-heterojunction architecture, a thin film perovskite layer could demonstrably be sandwiched by just hole and electron selective contacts, without any longer relying on complex nanostructuring (Figure 2.4) [34, 35].

Ever since, several different fabrication methods have been developed including a one-

step spin-coating method from solution precursors [17, 36, 37], a two-step sequential method [38], and vapor-phase deposition in a vacuum chamber [34] which have accompanied a phenomenal increase of PCEs.

Liu et. al demonstrated a landmark 15.4% efficient device consisting of a highly uniform vapour-phase deposited $\text{MAPbI}_{(3-x)}\text{Cl}_x$ perovskite layer incorporated in a planar heterojunction device, thus making the use of complex nanostructuring completely redundant [34]. The device further demonstrated a verifiably ambipolar charge transport activity, suggesting that perovskites are capable of delivering all basic modes of photovoltaic operation: from light absorption, charge generation up to the ensuing charge transport of electrons and holes across the device with close to unity internal quantum efficiency. Also, the sequential deposition technique shown by Burschka et al. allowed for better control of the resulting morphology and film reproducibility in MAPbI_3 -based devices, expediting an average PCE of 15% [38]. In 2014, Zhou et al. broke further barriers by carefully engineering interfacial layers in the device. By replacing the fluorine-doped tin oxide electrode (FTO) by indium-doped tin oxide (ITO) the amount of humidity during the fabrication of a $\text{MAPbI}_{(3-x)}\text{Cl}_x$ perovskite device could effectively be controlled [39]. In this case, the resulting improvements in terms of charge-carrier transport, extraction and the significantly strong suppression of charge-carrier recombination in the perovskite absorber itself, paved the way for a maximum PCE of 19.3% at an average of 16.6%.

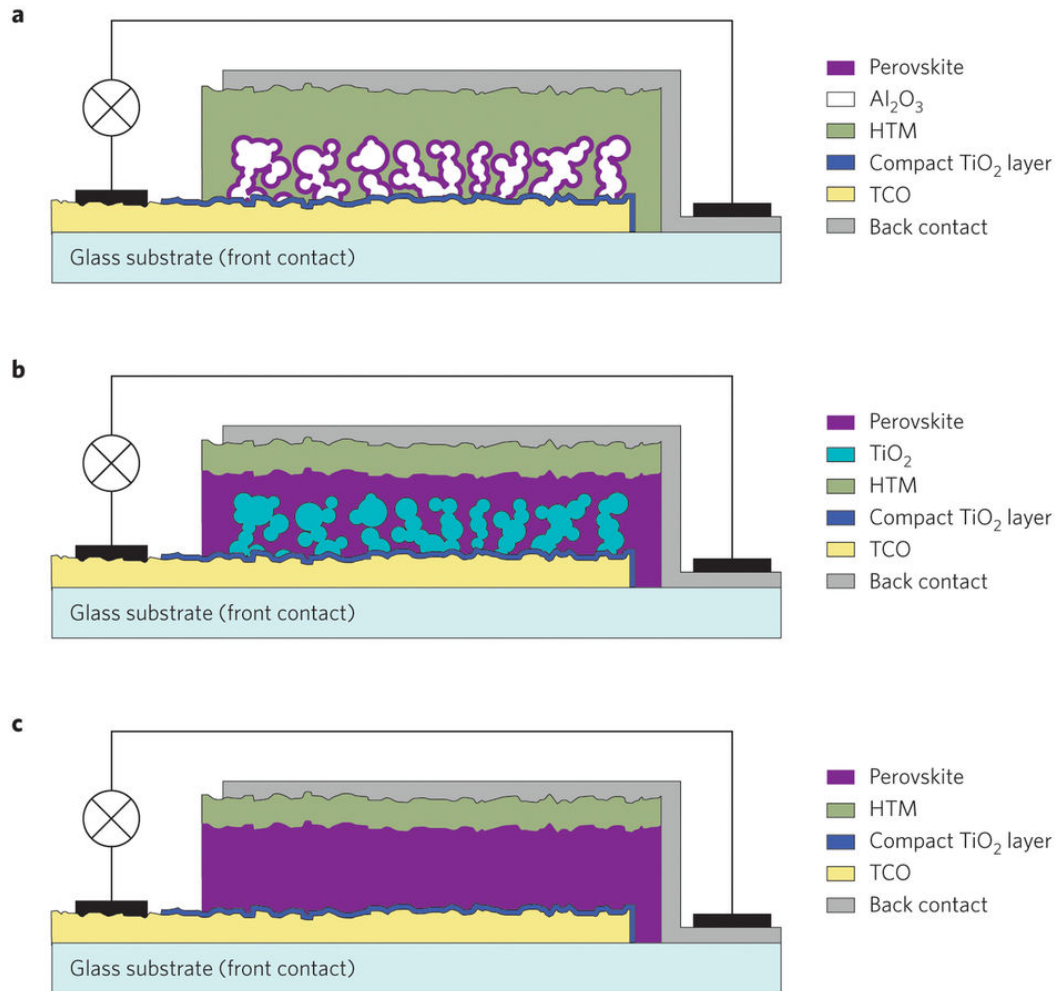


Figure 2.4: a) shows the device design of a ‘meso-superstructured’ OMHP solar cell device that uses a layer of Al_2O_3 nanocrystals overlaid by a MAPbI_3 perovskite film. The perovskite acts as a light harvester as well as an electron transporter. b) demonstrates how the perovskite infiltrates a mesoscopic TiO_2 scaffold which provides a nanostructured embodiment. The device structure is similar to a p-i-n junction solar cell formed by the HTM, perovskite layer and TiO_2 . The perovskite layer executes the role of both light absorber and hole conductor. c) displays the cross-section of a planar heterojunction solar cell finally omitting the inert mesoporous TiO_2 scaffold. Taken from reference [40].

2.2.3 Optimisation via Compositional and Interfacial Engineering

After the development of various film and device fabrication techniques that sparked skyrocketing PCEs, the next boost has been dominated by an interplay of rigorous device design, interfacial engineering and film processing on the one hand, and purely material-based compositional engineering of perovskite films, on the other. Single-cation perovskite compounds unveil an increasing inadequacy for reaching critical thermal and structural stability benchmarks with respect to making durable OMHP devices in future. For this reason, mixing of A-site cations have become an important design principle for manufacturing perovskite absorbers with improved thermal and structural stability. The motivation for using such mixed-compositional perovskite materials and a discussion of the fundamental mechanisms behind their improved stability is left for a more detailed discussion in Chapter 2.5.1.

Inspired by groundwork on the thermally more stable FAPbI₃ as an alternative to till then commonly used MAPbI₃ [41] - [18], Jeon et al. developed a mixed MAPbBr₃/FAPbI₃ composition in an endeavour to combine the advantages of both constituents in one solar cell. It turned out that the inclusion of just a small fraction of MA helps to significantly stabilise the room-temperature crystal phase of FAPbI₃. The resulting devices brought about a 17.9% PCE [43]. Baena et al. developed a MA/FA mixed-cation lead mixed-halide planar heterojunction device exceeding a PCE of 18% [44]. Using the same material composition, Bi et al. further elevated the PCE to 20.8% by adding excess PbI₂ to the precursor solution as a means to suppress nonradiative charge-carrier recombination channels [45]. Changing the material composition also enjoys an increasing popularity as a means of tuning the bandgap and alter optoelectronic properties, which directly impacts the PCE of devices as well. McMeekin et al. demonstrated a mixed-cation lead mixed-

halide $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite using the equally small but spherical caesium (Cs) instead of MA [46], part of which is presented in Chapter 5. In a single-junction device this perovskite composition brought about a stabilised PCE of 17% at a bandgap of 1.74 eV. Having thus strongly enhanced the almost non-crystalline (amorphous) single-cation $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ equivalent, this progress marks a noteworthy turning point [18]. In another push, Saliba et al. demonstrated the feasibility of triple and quadruple-cation OMHPs by adding Cs, or a combination of both Cs and the even smaller rubidium (Rb) cation, to the MA/FA mixed-cation perovskite lattice, ultimately prompting stabilised efficiencies of 21.1% and 21.7%, respectively [47, 48].

For further optimisation, Sang Il Seok and co-workers developed a new solvent engineering technology for the deposition of highly uniform perovskite layers, accomplishing a standardised PCE of 16.5% (under AM1.5 illumination, 100 mW cm^{-2}) [49]. In another approach, FAPbI_3 devices fabricated from intramolecular exchange of PbI_2 -dimethylsulfoxide(DMSO) with formamidinium iodide (FAI) exhibited even superior PCEs compared to those prepared from conventional PbI_2 , enabling a push to cross the 20% PCE boundary for the first time [50]. In a more recent work, a mesoporous titanium dioxide electron-transporting layer has been identified as an obstacle to light stability in MAPbI_3 . Replacing it by a superoxide-colloidal solution-route prepared Lanthanum-doped BaSnO_3 electrode increased the stability while further stepping up the PCE to 21.7% [51]. Eventually, Yang et al. managed to achieve striking 22.1% PCE by substantially lowering the concentration of deep-level defects by introducing excess iodine into the organic cation solution during the fabrication process of MAPbI_3 [52]. To date, this is the highest certified PCE of any metal-halide OMHP ever reported [6] and is comparable to that of other well-developed and commercialised solar cell technologies, such as multicrystalline silicon (c-Si, 21.3%), cadmium

telluride (CdTe, 22.1%) and copper indium gallium selenide (CIGS, 22.3%) [6, 53].

2.3 Perovskite Tandem Solar Cells

Apart from providing a bright outlook for the future of solar energy conversion, a rapid rise of OMHP device efficiencies at the same time raises the prospect for reaching a looming theoretical cap - the Shockley-Queisser limit for single-junction photovoltaic devices [54]. Blackbody radiation-related heat losses, charge-carrier recombination limited open-circuit voltage, and particularly spectral losses, subsume most of the efficiency losses incurred under device operation conditions. One way to disrupt efficiencies beyond the current performance metrics and the Shockley-Queisser limit, is to make so-called tandem solar cells: stacked ‘multi-bandgap’ materials where each layer absorbs a different spectrum of incident sunlight which can then be electrically collected through a variety of methods depending on the tandem configuration applied (discussed below) [55, 56].

Across the visible spectrum, perovskites have an easily tunable bandgap which renders them highly suitable for a variety of tandem solar cells systems, provided that an ideal current-matching of the stacked absorber layers is ensured by carefully choosing their respective bandgaps. In effect, this suggests perovskite-on-perovskite tandem solar cells as the best way forward. However, perovskite-on-silicon tandems could still leverage on the existing crystalline silicon manufacturing capacity, making them a top contender for a marketable tandem design that employs perovskite technology [57]. The design thereof, comprises of a low-bandgap silicon layer acting as a bottom-subcell and is overlaid by a wide-bandgap perovskite sub-cell on the top, that requires a band gap between 1.6 - 1.9 eV for excellent current-matching in a 4-terminal tandem configuration and ≈ 1.7 eV in 2-terminal tandems [58]. Finding suitable perovskite

materials that suffice this condition, constitutes a major incentive for conducting the work reported in this thesis. Recent reports on both perovskite-perovskite and perovskite-silicon tandem solar cells have demonstrated PCEs between 19-24% [59] - [62] and a stipulated potential for reaching 35% [63], far in excess of the Shockley-Queisser limit for conventional single-junction solar cells.

In keeping with Kirchhoff circuit laws, the PCE of a series-connected stack of an arbitrary number of sub-solar cells reaches its peak value when the short-circuit current (J_{SC}) of each sub-cell is equal, otherwise it will be limited by the lowest current [64]. On the other hand, the total open-circuit voltage (V_{OC}) is represented by the summation of each constituent subcell. Therefore, the integrated efficiency profile strongly depends on the bandgap of the top-subcell employed, with a forecasted peak performance for a 1.72 eV perovskite material [65].

An important type of perovskite tandem solar cells is the monolithic 2-terminal configuration which integrates two subcells through an intermediate transparent electrode, usually a silicon-based tunnel recombination junction diffused on top of a silicon bottom sub-cell emitter and a semi-transparent silver nanowire-based top electrode [57]. The junction facilitates electron tunneling from the electron-selective contact of the perovskite subcell into the p-type emitter of the silicon subcell.

Another established tandem solar cell configuration relies on connecting two independently fabricated units by mechanically stacking them on top of each other, commonly referred to as the 4-terminal design [66]. However, this configuration requires an additional transparent electrode and more processing steps causing increased levels of parasitic absorption and device fabrication costs, though has less stringent requirements on the bandgap of the top-subcell.

2.4 Scale-Up Technologies for Perovskites

Most of the highly efficient OMHPs setting new PCE records were only fabricated on millimeter-scale substrates in the research lab, leaving the production of similarly efficient large area devices as a major problem yet to be solved. The aim of scaling up OMHPs entails to achieve highly reproducible, uniform as well as pin-hole free perovskite films on larger areas. For this reason, many of the already thriving film fabrication techniques need to be improved to account for issues pertaining to scale-ups. Gu et al. used roll-coating for depositing a $\text{MAPbI}_{(3-x)}\text{Cl}_x$ film on a C3-SAM-modified PEDOT:PSS hole transport layer that makes the perovskite surface morphology smoother, ensuring a 5.1% efficient semi-roll-to-roll OMHP device [67]. Schmidt et al. applied slot-die coating and screen printing to make a MAPbI_3 thin film on flexible PET/ITO. Combined with a printed back electrode, such a fully roll-coated processing technique proved highly suitable for a low-cost scale up yielding a 4.9% PCE [68]. A vacuum flash-assisted solution process was recently developed for high-efficiency large-area OMHPs. With smooth and crystalline perovskite films of high electronic quality over large areas, solar cells with an aperture area exceeding 1 cm^2 reached a certified PCE of 19.6%. Conings et al. developed a complex-assisted gas quenching method, which uses nitrogen gas flow to remove residue solvent in order to form an intermediate DMSO-complex. It essentially serves as a solution deposition method to make highly reproducible and pin-hole free perovskite layers, reaching a 18.0% PCE [69]. Ye et al. developed a soft-cover deposition method to make pinhole-free MAPbI_3 perovskite films with large grain sizes on an area as large as 51 cm^2 [70]. This technique ensured a material utilization efficiency of up to 80%, strongly exceeding results obtained from spin-coating. It further ensured a reproducible PCE of 17.6% in 1 cm^2 large solar cells and proved suitable for a variety of large-area coating procedures.

2.5 Stability of Perovskites

Despite the success story of OMHPs in the research lab, arguably the most pressing issue to address before commercialisation is long-term stability. Most of the reported devices only hold on to their stability and peak efficiency for hours, if not minutes. In comparison, most silicon solar panel manufacturers confidently issue 20-year warranties with the promise to retain at least 80% of the rated power after 20 years of use. As of today, a lot of progress has been made with respect to enhancing the long-term stability of perovskites, while many other challenges are yet to be overcome.

2.5.1 Structural Stability

As pointed out in Section 2.3, intrinsic perovskite stability is contingent on the given material composition and its impact on the lattice structure and crystal phase preferences. The challenge is threefold, since instabilities may arise from changes in crystal structure, chemical decomposition, or de-mixing (such as halide-segregation). For instance, the most widely studied MAPbI_3 undergoes a structural phase transition above 55°C [8], and degrades quickly upon exposure to moisture, air and heat above 85°C [71]. Alternatively, FAPbI_3 offers improved thermal stability and a reduced band gap closer to the optimum value for single-junction solar cells. However, FAPbI_3 is prone to a structural instability at room temperature, transforming from the photoactive ‘black’ perovskite α -phase into a photo-inactive ‘yellow’ non-perovskite hexagonal δ -phase aided by the presence of solvents and humidity [33, 43]. Alternatively, all-inorganic perovskite solar cells employing caesium (Cs) as the A cation have been explored [72, 73]. Because of the smaller ionic radius of the Cs cation [42] - $1.81 \text{ \AA}$ as compared to $2.70 \text{ \AA}$ for MA and $2.79 \text{ \AA}$ for FA - the bandgap of

CsPbI₃ widens to 1.73 eV, within the optimum range of 1.7 to 1.8 eV for a top-subcell material in tandem with a crystalline silicon bottom solar cell [74]. However, the photoactive black α -phase of CsPbI₃ only crystallises above 300°C while at lower temperatures the material reverts back to a photo-inactive yellow orthorhombic δ -phase [33, 73]. Nonetheless, mixed-halide CsPb(Br_xI_(1-x))₃ materials show significantly better resistance under heat stress [75] and enhanced photo-stability [76] compared to their MA and FA-based counterparts.

Such differing causes of instability triggered an intense research strand to create stable alloys, that is, to use A-cation intermixing to create hybrid perovskites devoid of thermal or structural instabilities [77, 78, 79]. For example, initial attempts to substitute small amounts of FA with MA in FAPbI₃ were shown to stabilise the perovskite phase and yield higher PCEs, resulting from the stronger interaction between the more polar MA and the PbI₆ octahedral cage [80]. However, mixed-cation FA/MA perovskites still retained a propensity towards decomposition and degradation under heat stress and humid environments [10, 43], which is probably caused by the relatively volatile nature of methylammonium [71]. A promising recent avenue has been the partial substitution of Cs for FA, MA or MA/FA for which substantial enhancements of the PCE and photo- and moisture stability were found by a range of groups [77, 78, 79]. Li et al. argued that the effective ionic radius of the Cs/FA mixture can be used to fine-tune the Goldschmidt tolerance factor towards structurally more stable regions [81]. Saliba et al. has demonstrated triple-cation perovskite solar cells with stabilised efficiencies up to 21%, suggesting that the addition of Cs to MA/FA mixed cation perovskites significantly stabilised the α -crystal phase of the perovskite by eliminating remnant non-perovskite phases and impurities [47]. More recently, Song et al. managed to demonstrate highly efficient triple-cation OMHPs compatible with a ZnO electron transport layer, which earlier failed in combination with thermally unstable MAPbI₃ [82].

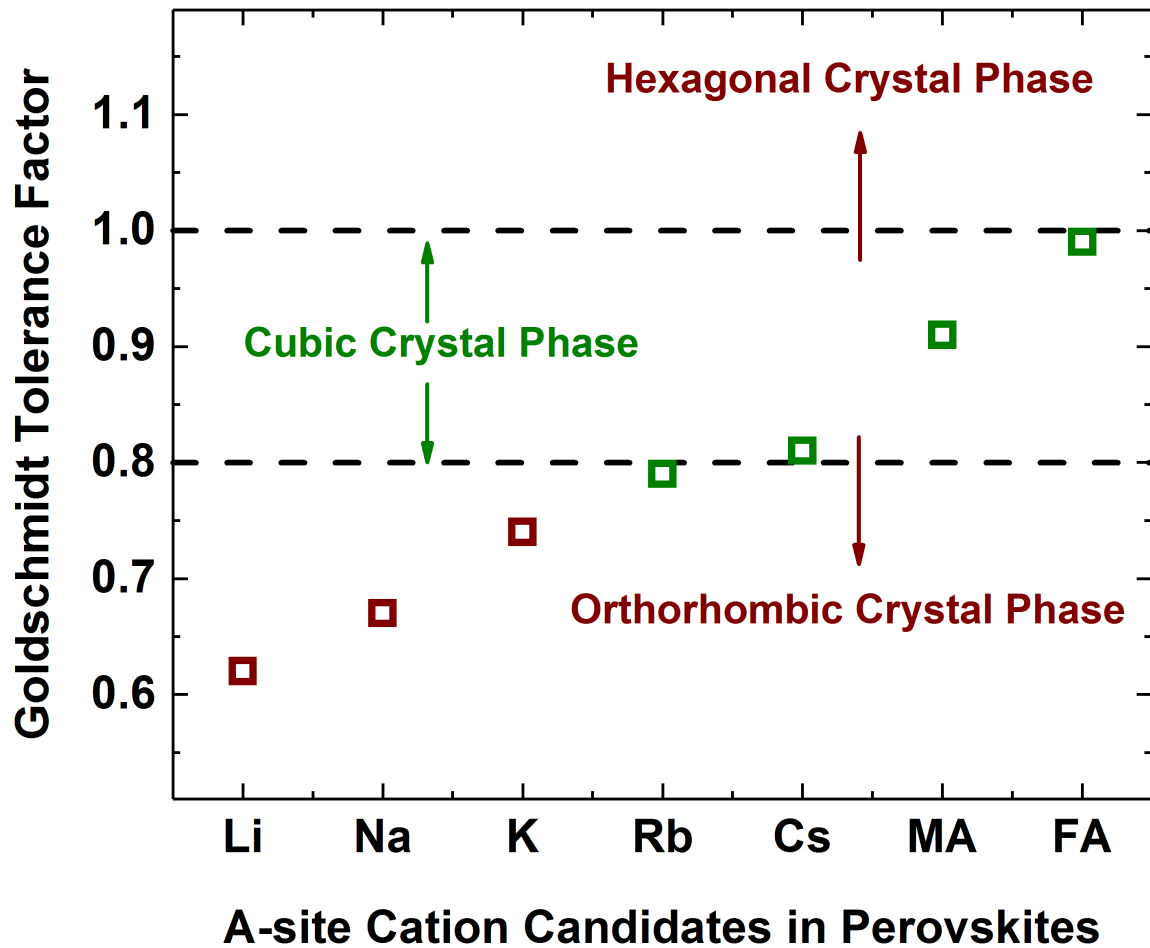


Figure 2.5: Tolerance Factors of oxidation-stable A-site cation candidates in perovskite structures. Practically, perovskites with a tolerance factor between 0.8 and 1.0 show a photoactive black phase (open green squares). This area is bound by black, dashed horizontal lines in the graph. Below and above this range non-photoactive crystal phases emerge (brown open squares). While MA appears as the most suitable candidate, Rb, Cs and FA display ample potential for integration in the perovskite lattice to make up for structural and thermal weaknesses of MA. Tolerance Factor calculations and ionic radii were taken from reference [48].

2.5.2 Ambient Air Oxygen

Atmospheric air has been reported as having adverse effects on the perovskite layer and also on solar cell device components, such as charge transporting layers, where the influence of oxygen and water vapor evidently induce material decomposition and degradation in for example MAPbI₃ films [83]. In presence of oxygen, incident light promotes a decomposition pathway in the perovskite, which could not be observed in dark or inert atmosphere [84]. This points towards a photo-oxidation process involved in the decomposition of the perovskite, shown to happen within just a few hours under full AM1.5 illumination in air. Aristidou et al. also finds an explanation in the role of the acidity of the organic cation MA [85]. In 2012 and 2013, the introduction of solid-state hole conductors and controlled sequential deposition methods laid the foundations for improving the operational stability in ambient conditions from just 10 minutes to 500 h [30, 38]. Compositional variation by means of A-site cation mixing in the perovskite, however, seems to be a much simpler method for attaining atmospheric stability, because it stabilises the crystal structure of the material. Substituting MA with FA and the inorganic Cs results in a remarkable stabilisation of the operational lifetime by more than an order of magnitude in a mixed-cation Cs_{0.17}FA_{0.83}Pb(I_{0.6}Br_{0.4})₃ film [86]. Encapsulating solar cells is considered another handy way to seal the perovskite absorber from detrimental effects in ambient air, though it brings along an additional cost factor. Therefore, it can be inferred that realising an excellent trade-off between structural stabilisation of the perovskite compound and device encapsulation, provides the brightest prospects for a medium-term solution of making operational OMHPs.

2.5.3 Ambient Air Moisture

Compared to oxygen, the effects of moist air are of more grave concern, given its ability to rapidly and intensely trigger decomposition in the perovskite. Moisture seems to have two distinct avenues for influencing the perovskite: Firstly, during the fabrication process where it can even aid film formation and crystallisation, if effective control over ambient humidity levels is exercised. Contrary to this, after film fabrication, storing samples in a locally humid environment presents a one-way road for causing irreversible degradation of the film, as evidenced by multiple reports with respect to the commonly explored MAPbI₃ [87] - [89]. The mechanism of degradation is thought to involve the formation of hydrated intermediate structures as a result of the water vapor's ability to easily penetrate the perovskite lattice. After forming hydrogen bonds with the acidic organic cation MA [90], a totally irreversible degradation to PbI₂ is promoted [91]. Yet again, compositional variation of the perovskite compound raises hope for impeding the detrimental effects of moisture. Incorporating bromide at the X-site reduces the lattice parameter and enhances the hydrogen bond between the MA cation and the lead halide octahedra, somewhat blocking out water vapor pathways into the perovskite lattice [37]. Tuning the A-site cation also improves moisture stability: Park and co-workers demonstrated that a mixed-cation Cs_{0.15}FA_{0.85}PbI₃ film sustained its absorption stability four times longer than single-cation counterpart FAPbI₃ [79], while Snaith and co-workers even managed to keep a Cs_{0.17}FA_{0.83}Pb(I_{0.6}Br_{0.4})₃ film stable for over 650h under AM1.5 illumination at ambient air [86]. Of late, Sun et al. achieved excellent air-stability and crystallinity by incorporating a Pb(SCN)₂ additive in FA/MA/Cs triple-cation perovskites, thus also obviating the need for a thermal annealing protocol [92].

2.5.4 Photo-Induced De-Mixing in Mixed-Halide Perovskites

Having discussed chemical decomposition and the crystal structure as the two main sources of insufficient stability in perovskite films, a third source involving perovskite ‘de-mixing’ has recently been receiving a great deal of attention. Hoke et al. reported the phenomenon of reversible photo-induced transformation of steady-state photoluminescence (PL) spectra for mixed Br-I perovskites, which voiced concerns regarding the photo-stability of mixed-halide materials [93]. Under continuous illumination, $\text{MAPb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites with high bromide fractions were observed to create a new dominant PL peak at around 740 nm, that is effectively red-shifted toward the emission spectrum of a very iodide-rich $\text{MAPb}(\text{Br}_{0.6}\text{I}_{2.4})$ perovskite. It was suggested that photoexcitation of lead mixed-halide films triggers halide-segregation into two different crystalline phases, that is, an iodide-rich minority domain and a bromide-rich majority domain. This instability poses a serious threat for the performance of solar cell devices using bromide-rich lead mixed-halide layers. This is mainly because the open-circuit voltage may then become limited by the energy of the lower bandgap phases. The funneling of charge-carriers to low-energy regions, reduces the nonradiative recombination rate because locally the charge-carrier density is enhanced. In turn, this mechanism leads to the filling of traps and increase in bimolecular recombination of electrons and holes [94].

After removing the light source the PL spectrum was observed to return to the pre-illumination state within minutes. Furthermore, Hoke et al. observed XRD peak splitting of these materials under direct light illumination corroborating the assumption of domain splitting into an I-rich minority and Br-rich majority phase [93]. Regardless of the applied characterisation method to track down phase segregation, $x < 0.2$ appears to be the most stable domain for bromide-iodide lead mixed-halide perovskite compositions varying between $x = 0.3$ [95] and $x = 0.9$ [96]. Figure 2.6

provides an overview of a range of lead mixed Br-I perovskite materials that have been tested for their tendency to exhibit photo-induced halide-segregation [97]. The initial PL peak energy for all listed material compositions is different based on the respective A-site cation alloyed in the perovskite structure, ranging from ≈ 1.9 eV for Cs-based perovskites to ≈ 1.55 eV for MA/FA cations. Nonetheless, the figure clearly pinpoints the independence of this phenomenon from the initial PL peak energy, with all films equally shifting towards their respective iodide-rich domains ($x \approx 0.8$), corresponding to roughly 1.7 eV for most them. Interestingly, structurally more stable mixed-cation Cs/FA and all-inorganic CsPbX₃ films have a tendency to be more resilient against photo-induced halide segregation. This clearly suggests a non-intrinsic nature of this phenomenon [46, 76], which is further discussed in Chapters 5.2.1 and 6.2.1.

However, the underlying physical and chemical mechanisms that drive this effect are still not precisely known, though numerous possible explanations have been brought forward. The sudden occurrence of low-energy PL peaks under light illumination have also been observed in very low temperatures [93, 94], which deems a dominant role of any heat-induced phase segregation as unlikely, though the generally low heat conductivity of perovskite materials makes it difficult to preclude the role of local heating in this context [98].

With regards to the light intensity applied for illuminating the mixed-halide perovskites, a lucid explanation is still lacking. On the one hand, some reports present photo-induced halide segregation as completely independent from incident light intensity due to similar PL shift dynamics obtained for laser intensities orders of magnitude apart [93], while others have tried to determine threshold powers [99] or simply are unable to detect this effect at intensities in the range of lower mW cm^{-2} units, as described later in Chapter 4.2 of this work.

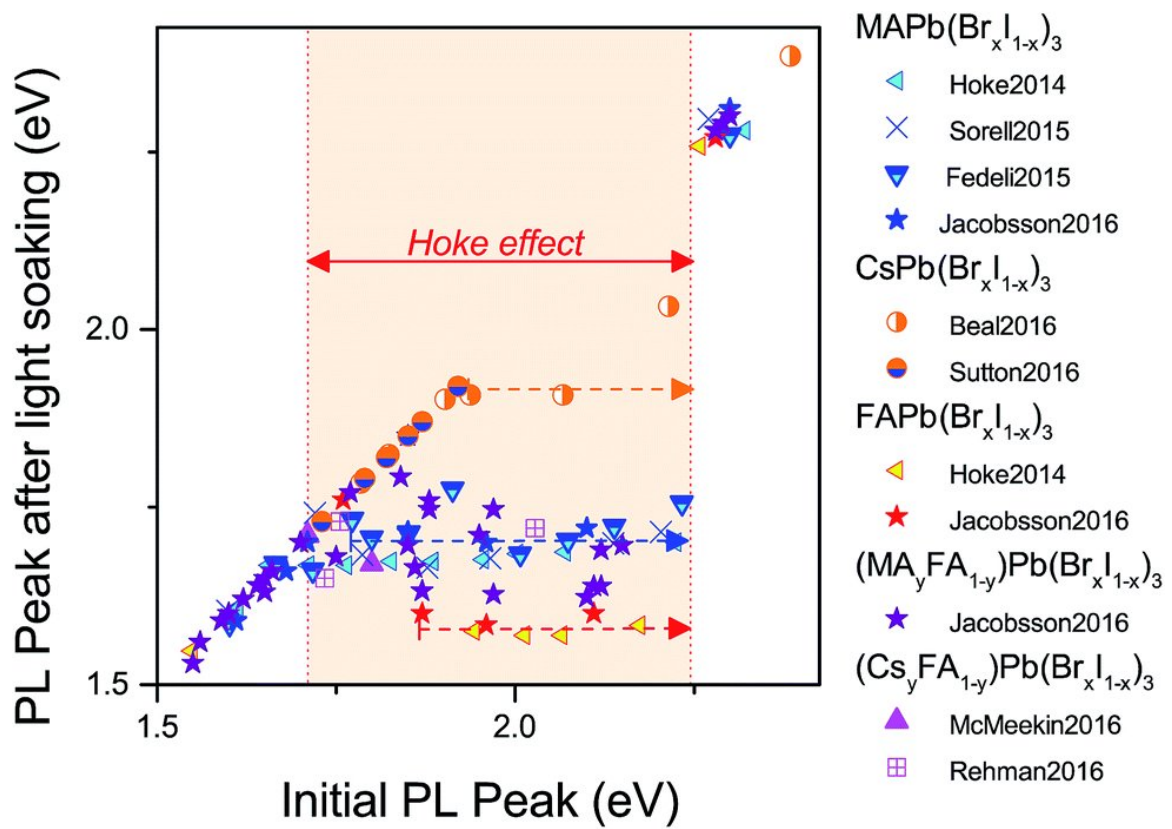


Figure 2.6: Visualisation of PL stability observations in multiple Br-I mixed-halide perovskite material compositions measured from 2014 to 2016. The PL peak energy (eV) is depicted as a function of the initial (pre-illumination) PL peak energy. Taken from reference [97].

Furthermore, the influence of varying excitation wavelengths has been thoroughly investigated by Barker et al. Ensuring a similar flux of incident photons by adjusting laser intensities for each wavelength tested, a longer-wavelength light appeared to slow down phase-segregation on the time scale [94]. However, the different dynamics have been attributed to different absorption profiles of light carried by different wavelengths and energies.

In another work, Yang et al. rather ascribed the applied laser repetition rate as a major facilitator of halide phase-segregation. At a fixed laser intensity and illumination time, tuning the frequency from 500 Hz to 1 MHz altered the dynamics of PL shifts significantly, with no PL shifts observed for frequencies below 500 Hz [100]. At higher frequencies in the MHz range, photogenerated charge-carrier populations are able to hold out for long enough in order to trigger this effect. The existence of such a correlation has been confirmed by Barker et al., who suggest defect-assisted migration of halide ions away from the illuminated film surface as a plausible explanation [94]. Apart from photo-induced phase-segregation, many groups report problems with the tunability of Br-I mixed-halide perovskites across the entire range, with the occurrence of either phase gaps [18] or drastically increased energetic disorder [93, 101] in the range between $x = 0.3$ and $x = 0.6$. This raises the question of an intrinsic miscibility gap, in phase-transitional regions of solid mixed-halide solutions because of changes in the Helmholtz free energy after photoexcitation [94]. However, this idea is put into question, since it does not explain the facile reversibility of such phase-segregation [93] without the input of external energy.

2.6 Optoelectronic Properties

The remarkable efficiencies of OMHP devices are strongly correlated with highly favourable optoelectronic properties of the perovskite absorber layer which have been studied more extensively in recent years [102, 103]. In addition to high optical absorption coefficients in the range of 10^5 cm^{-1} in the visible range [11, 53] and high charge-carrier mobilities, bimolecular charge-carrier recombination rates defy the Langevin limit for kinetic recombination by at least four orders of magnitude [104, 105]. MAPbI_3 also appears to exhibit only shallow trap-levels and although the grain boundaries have recently been shown to induce nonradiative decay [106], regions only a few tens of nm away from the grain boundaries appear to be unaffected [107, 108]. All of these properties contribute to high open-circuit voltages, long charge-carrier lifetimes of at least tens of nanoseconds, and micrometer diffusion lengths, which are crucial for planar-heterojunction photovoltaics [109]. Nonetheless, these parameters are also expected to depend on the influence of crystallization conditions on perovskite morphology in fabricated films [110].

2.6.1 Electronic Structure of Perovskites

As pointed out in Chapter 2.1, the chemical variation of a perovskite composition gives way for structural phase transitions via octahedral tilting. These have the potential of significantly modifying the energy band structure of the material, which has been investigated with density-functional theory calculations [111, 112] and confirmed by experiments. Here, the bandgap of multiple perovskite compositions could be dictated by simply varying X-site halide anions, a procedure that alters the metal-halide bond length [18]. The electronic structure close to the band edge is mainly controlled

by the BX_6 building blocks [113, 114], and by implication, a changing energy band structure alters the optoelectronic properties and charge-carrier dynamics. Moreover, the rotation of the organic cations, MA or FA, has been reported to cause changes in the lead-halide bonding, which also contributes to the modification of the band structure in hybrid perovskites [115].

In case of the commonly explored MAPbI_3 , the valence band is dominated by p-states of I and contributions from antibonding I p- and Pb s-states, while the conduction band is almost completely made up of Pb p-states [114, 116, 117]. This is in good agreement with most classes of ionic materials, where the valence band is dominated by electronic states of the anion and the conduction band by those of the cation [118].

2.6.2 Charge-Carrier Transport Properties

So far, many investigations have been conducted to elucidate the nature of photoexcited charge-carriers in OMHPs as to whether bound electron-hole pairs (excitons) or free charge-carriers are the predominant species present. Ideally, the thermal energy at room temperature ($k_B T = 25.8 \text{ meV}$) is larger than the energy of a bound state which is dictated by the Coulombic interaction between electrons and holes. If this is given, the photoexcited charge-carriers are able to contribute instantaneously to the photocurrent without the need of any additional precautions to take for dissociating excitons. Contrary to OPVs and DSSCs, there is increasing agreement that this condition may hold true for OMHPs, with free charge-carriers being the primary species produced after photoexcitation at room temperature. This has been evidenced by pertaining derivations from multiple ultrafast spectroscopic investigations, such as photoluminescence and band-edge dynamics measurements [27], [119] - [123], however, with values strongly fluctuating between 2 – 62 meV [13]. It is important to

understand this differentiation as it significantly drives the nature of recombination mechanisms and excited state dynamics that can be measured by transient photoluminescence and terahertz spectroscopy explained in more detail in Chapter 3. The different contributions to the recombination dynamics in a semiconducting material can be subsumed under trap-assisted *monomolecular recombination* k_1 , band-to-band *bimolecular recombination* k_2 and the higher-order *Auger recombination* k_3 . An explanation of the underlying mechanisms is provided in Figure 2.7 [13].

Furthermore, OMHPs exhibit remarkably sharp absorption onsets which are well-reflected in low Urbach energies extracted from near band edge optical absorption measurements [124, 125]. Urbach Energies also serve as a benchmark for crystalline phase stability, indicating disorder and the sharpness of band edges.

The electron and hole effective masses are inversely proportional to the curvatures of the conduction and valence band and constitute between 10-15% of the free electron mass m_0 , comparable to prototypical inorganic semiconductors such as silicon or GaAs [126, 127]. Such similarities to inorganic semiconductors in terms of electronic structure and charge transport may suggest that photoconductive OMHP materials have a likely potential to approximate charge-carrier mobilities of at least a few hundred square centimetres per volt per second in near future [128]. However, most previous charge-carrier mobility measurements from various highly efficient thin-film perovskites (MAPbI_3 , $\text{MAPbI}_{3-x}\text{Cl}_x$) show mobilities of tens of square centimetres per volt per second [104, 129]. Despite similar electronic and material properties, this shortfall clearly raises the question of intrinsic limitations in OMHPs as compared to their inorganic counterparts.

Nonetheless, the suitability of OMHPs as active absorbers is reinforced by extraordinarily low recombination rates defying the predicted Langevin-ratio by many orders of magnitude, which suggests that the charge-carriers are potentially able to quickly diffuse through the active material and easily reach the electrodes for efficient extraction

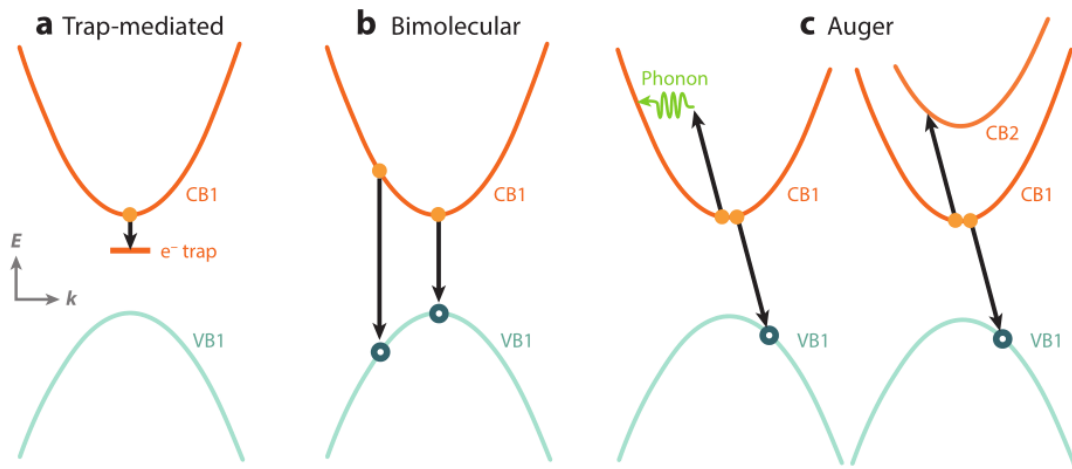


Figure 2.7: A schematic illustration depicting recombination mechanisms operating in OMHPs. a) Monomolecular (nonradiative) recombination k_1 as a trap-mediated process involving the capture of either an electron or a hole in a trap (defect) state. Usually k_1 can be controlled by better material processing. b) Intrinsic bimolecular recombination k_2 directly between electrons and holes, from either relaxed states or states higher up in the band. (c) Auger recombination k_3 is a higher-order process that becomes relevant only at high charge-carrier densities. It is a many-body process involving at least three charge-carriers, where the energy of a recombining electron-hole pair is not emitted instantly, but transferred to another electron in the conduction band which then thermalizes back to the edge of the conduction band [13].

[105]. The origins of such low recombination rates in OMHPs have been discussed widely in the literature. Initially, it was assumed that preferential localization of electrons and holes within the perovskite lattice leads to a reduction of the spatial overlap of the respective wave functions, thereby lowering the probability for charge-carriers to meet and recombine [129]. However, this kind of ‘self-trapping’ of electrons and holes in their respective bands is supposed to entail the presence of electron-phonon coupling or polaronic effects [130, 131]. Such polaronic effects seem to be negligible though, given the relatively small Stokes shift between absorption onsets and PL emission peak energies observed in these systems at room temperature. On the other hand, indications for a coupling of photogenerated charge-carriers and phonon modes seem plenty, as e.g. demonstrated by the homogeneous broadening of PL linewidths in $\text{MAPbI}_{3-x}\text{Cl}_x$ systems [132] and modulations of lead-halide vibrations found in frequency-domain THz photoconductivity spectra of MAPbI_3 at 80K [133]. At such low temperatures, obvious deviations from the ideal Drude model clearly suggest a reduction of electron-phonon interaction due to reduced mode occupancy [102]. In turn, this also suggests that room-temperature mobilities measured in the range of $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for MAPbI_3 systems most likely reflect intrinsic band-transport properties in conjunction with scattering off phonons, rather than extrinsically contributing factors like material crystallinity or impurity [131]. As matters stand, these considerations recommend the view that charge-carrier mobilities at room temperature may have already reached an intrinsic upper limit.

The diffusion lengths of both luminescent and photo-induced charge-carriers in single-cation lead tri-halide perovskite materials have been specified in the micrometer range [109, 134]. Although, this is a formidable improvement compared to other established solution-processed light-harvesting technologies (such as OPVs and DSSCs), strong fluctuations due to varying material purity and crystal grain sizes make it challenging to pinpoint the performance level of films composed of the same material

composition [135, 136]. Therefore, controlling trap-state densities (and associated trap-related monomolecular recombination) is pivotal for ensuring balanced charge-carrier diffusion in thin film perovskites. Some reports suggest that polycrystalline films are affected more severely due to large concentrations of defect states in grain boundaries [106, 137]. Essentially, grain boundaries can be described as ‘breaks’ in the crystal structure causing the formation of neighbouring crystallites with different orientation and size. For many established photovoltaic technologies such as CdTe, polycrystalline silicon and CIGS, these grain boundaries hold a sway in determining charge-carrier dynamics [138] - [141]. Since perovskites are different to these inorganic semiconductors because of lower doping levels and the presence of defect states, the effect of grain boundaries on their photophysical properties is yet to be clarified [142, 143].

Chapter 3

Experimental Techniques

The work reported in this thesis explores the early-time dynamics of photoexcited charge-carriers (electrons and holes) in thin-film OMHP absorbers. Indispensable insights into ultrafast charge-carrier recombination rate constants and charge-carrier mobilities in the context of a diverse range of alloyed perovskite systems are provided for which the application of state-of-the art spectroscopic techniques was required. Spectroscopy with radiation in the THz frequency range has taken root as a reliable tool that enables the probing of photoexcited mobile charge-carriers inside photoconductive materials. The transient response of charge-carriers in a material can be probed with a short pulse as a function of time-delay after optical photoexcitation. Particularly suitable is the use of an optical-pump terahertz-probe spectroscopy (OPTP) setup, which records the transient photoconductivity response caused by photogenerated charge-carriers probed by a short pulse of THz radiation incident on the sample at preset time-delay intervals with regard to the optical pump pulse. Ultrafast photoluminescence spectroscopy helps to track light emission (fluorescence) caused by the relaxation of photoexcited electrons and provides insights into characteristic radiative decay processes in the material under study. Additionally monitoring the photoluminescence intensity as a function of time after short-pulsed photoexcitation, gives crucial information on the lifetimes of photoexcited charge-carriers. The following subsections lay out details concerning the experimental design of above-

mentioned techniques and conclude with elaborate descriptions of associated data analysis steps and the fundamental physics behind them.

3.1 THz Spectroscopy

Since the arrival of the laser in the 1960s, it has emerged as a powerful source of monochromatic, coherent, pulsed or continuous-wave radiation, thereby increasing the overall popularity of optical spectroscopy as a useful tool for material characterization. Spectroscopy, in a broad sense, is the study of electromagnetic radiation interacting with matter. The radiant energy transported in form of propagated electromagnetic waves can be absorbed, emitted or scattered by atoms and molecules and reveal important characteristics of underlying electronic structures, the spectral response of which varies depending on the frequency range of the applied radiation source [144, 145]. Being in between the microwave and infrared range of the electromagnetic spectrum, THz waves occupy the frequency interval from 0.1 to 20 THz [146]. This is similar to where optical signatures of mobile charge-carriers can usually be found and thus presents an effective means to investigate the recombination dynamics and mobilities of charge-carriers in photoconductive materials through the measurement of the change in THz radiation transmittance inside the material [147]. Although, microwave-based spectroscopy as another intrinsically sensitive technique to mobile charge-carriers has been a commonly applied method for probing their dynamics, *THz spectroscopy*, as an emerging alternative, enables a higher time resolution bringing about the possibility to analyse ultrafast processes down to the time scale of only a few picoseconds.

3.1.1 Optical Pump - Terahertz Probe Spectroscopy

In OPTP spectroscopy a sample is excited by an ultrashort laser pulse and followed by a single-cycle THz probe pulse, which transmits the sample only after a well-defined time-delay [131]. For photoconductive materials, the obtained transient over a successive time-delay range displays changes in the electric field amplitude of the transmitted pulse, which in turn reflects the decay dynamics of photoexcited charge-carriers. Hence, this experimental setup offers an adequate means to actively time-resolve decay patterns or changes in the photoconductivity of the samples under study. The following sketch provides a schematic depiction of the working mechanisms in an OPTP setup and is applied for all upcoming experiments pertaining the study of decay dynamics of photoexcited charge-carriers in perovskites (Figure 3.1).

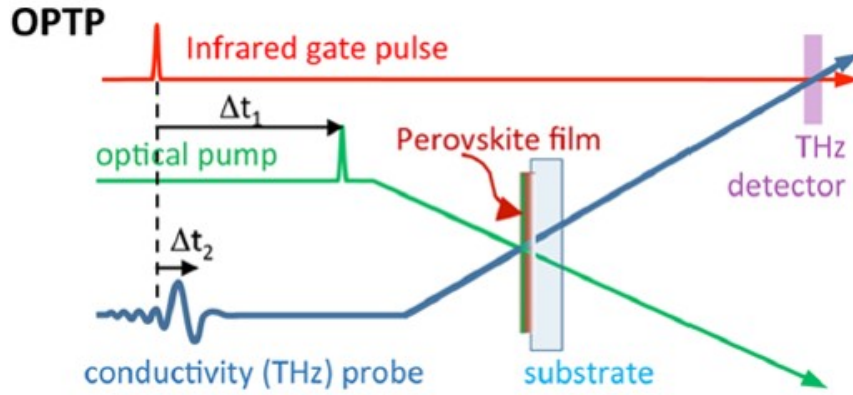


Figure 3.1: Schematic representation of the optical-pump THz-probe setup's operation principles used in this work. The ultrashort pump pulse (green) excites significant charge-carrier populations in the perovskite film coated on the substrate, while a single-cycle THz-probe pulse (blue) transmits the film after a short time-delay and subsequently overlaps with the infrared gate-pulse (red) for signal detection behind the sample. Taken from Reference [131].

3.1.2 THz Generation

Multiple different methods are available to generate THz pulses from ultrafast and short laser pulses. Amongst others, the use of photoconductive antenna, utilization of emission from transient photo-Dember fields or built-in surface states in semiconductors [148], and non-linear optical rectification are commonly available and differ from each other mainly in bandwidth and intensity of the emitted THz pulse [149]. Photoconductive antennae apply transient photocarriers to generate THz pulses, whereas built-in surface states formed by the band bending area in certain semiconductors, such as GaAs, have also successfully demonstrated the generation of THz radiation. THz generation from the above mechanisms use photo-induced carriers, while in second-order non-linear optical rectification the process is driven by ‘virtual carriers’ induced by optical excitation from very short laser pulses. Comparatively, this method offers the advantage of generating THz pulses with suitably broad spectral bandwidths and for this reason it has been witnessing an increased popularity for use in time-resolved THz spectroscopy setups like OOTP, enabling the investigation of mobile charge-carriers in semiconducting materials. THz pulses are produced via optical rectification of femtosecond laser pulses in a non-linear medium like an electro-optic crystal [150, 151]. Historically, Shen and co-workers were amongst the first to observe far-infrared radiation generated by picosecond pulses in LiNbO₃ crystals [152]. Usually, the THz pulse contains many frequency components and when it interacts with the electro-optic crystal, THz emission-inducing wave-mixing between two frequencies ω_1 and ω_2 occurs, including but not limited to sum-frequency generation, $\omega_1 + \omega_2$, and difference frequency generation, $\omega_1 - \omega_2$. For THz generation only the latter is relevant, with difference frequency mixing of all frequencies within the bandwidth $\Delta\omega$ of a near-infrared femtosecond laser pulse, the bandwidth of which in turn determines the bandwidth of the generated THz pulse [153], [154]. In the OOTP spectroscopy

setup used in this work, THz pulses are generated in a non-centrosymmetric 0.45mm thick $\langle 110 \rangle$ GaP crystal, which produces a THz bandwidth of up to 3.3 THz from incident femtosecond laser pulses coming from a regenerative Ti:sapphire amplifier [155] - [157].

3.1.3 THz Detection: Electro-Optic Sampling

For the detection of broadband THz waves there are again numerous established ways depending on the desired purpose of usage. These include photoconductive antennae [158], electric-field-induced second-harmonic generation in laser-induced air plasma [159], asynchronous optical sampling and free-space electro-optic sampling [160]. In the OOTP setup applied in this work, the latter method of electro-optic sampling is used, because it yields the best trade-off between the obtained sensitivity and the broadness of the bandwidth [161]. Additionally, this setup involves a very short optical sampling pulse (gate pulse), which overlaps with the THz pulse before both run into the non-linear electro-optic crystal. The detection in the crystal is based on the linear electro-optic effect (Pockels effect), which basically describes how the externally applied electrical field created by the gate pulse causes birefringence in the electro-optic detector crystal, the extent of which is proportional to the electric field of the incident THz pulse [162]. Subsequently, this effect induces a rotation in the polarization of the gate pulse, the magnitude of which is in turn proportional to the magnitude of the THz electric field amplitude and sign. In this way, it is possible to map out the entire THz waveform in the time-domain by merely varying the time-delay between the overlapping gate and THz pulse [163]. The selection of a suitable electro-optic detection crystal and its thickness is contingent upon the desired trade-off between its frequency response and sensitivity. A thicker crystal leads to

a longer interaction length, which upon increasing total polarization of the crystal, improves the signal-to-noise of the detection, while it simultaneously implicates a reduction of the THz bandwidth due to group-velocity mismatch [156, 164]. In a very thin crystal, on the other hand, the interaction window in the time-domain is limited, which significantly impedes the frequency resolution of the measurement. To minimise adverse effects from both ends, a combination of a thick crystal with an inactive orientation (e.g. $\langle 100 \rangle$) and a thin crystal of the same material with an active orientation (e.g. $\langle 110 \rangle$) can be assembled. Therefore, in this work, THz detection is achieved by means of a 0.2 mm thin $\langle 110 \rangle$ ZnTe crystal fused on top of an inactive 3 mm thick $\langle 100 \rangle$ ZnTe crystal.

3.1.4 Optical-Pump THz-Probe Experimental Setup

Figure 3.2 displays a detailed sketch of the OPTP setup used for all charge-carrier dynamics experiments performed in this work. The centrepiece of operation is a 1.1 kHz-repetition rate amplified Ti:Sapphire laser (Spitfire), which generates 800 nm laser pulses of 40 fs duration each. The Ti:sapphire laser consists of a rod of Ti:sapphire (titanium-sapphire), which is pumped by an external continuous-wave Nd:YLF laser source [9]. The pulse generated by the Ti:Sapphire amplifier is then split into three different pathways by using dielectric beam splitters.

- **Optical Pump Pulse:** 50% of the output energy contained in the 800 nm laser is used as a pump beam to optically excite charge-carriers in the samples under study. Furthermore, by using a beta-barium-borate frequency-doubling crystal the pump laser is converted into a 400 nm pulse to guarantee above-bandgap excitation in all perovskite films under investigation. Before the frequency is

doubled in the optical path, the pump beam also passes through a rotating chopper wheel (C1), phase-locked at a frequency of 27.5 Hz.

- **THz Probe Pulse:** Another 50% of the output is used as an optical source medium to generate single-cycle THz pulses in a 0.45mm thick $\langle 110 \rangle$ GaP electro-optic crystal. Before the generation of the THz pulse via non-linear optical rectification, the forerunning optical pulse passes through chopper C2 phase-locked at a frequency of 550 Hz, which equals half the repetition rate of the amplifier and is thus significantly higher than the pulse frequency of the pump beam.
- **Optical Gate Pulse:** A very small percentage of the original 800 nm pulse is diverted for use as a gate pulse that measures the THz electric field by means of free-space electro-optic sampling in a ZnTe crystal.

The setup further employs finely tunable motorized stages where the time-delay between pump-, probe- and gate-pulse can be adjusted mechanically by enlarging the optical path length of a chosen beam. The resulting range lies between a few femtoseconds and goes up to 2.5 nanoseconds. The procedure of THz pulse generation and detection takes place in an enclosed and vacuum-sealed box in order to minimise THz absorption by water vapor [163]. The first stage in the path of the probe beam after entering the box is the THz emitter, where the THz pulse is generated [9]. A PTFE beam blocker stops remnant optical pulse components to traverse further, while it allows the single-cycle THz pulse to transmit unhindered and without any attenuation. Subsequently, two successive gold-coated off-axis parabolic mirrors collimate and focus the THz onto the sample after it has successfully overlapped with the optical pump pulse, which enters the box via lens L1, that enables the control of its beam profile diameter such that it becomes large enough to exceed the profile of the THz pulse. It should be noted, that the THz pulse interacts with the sample at a

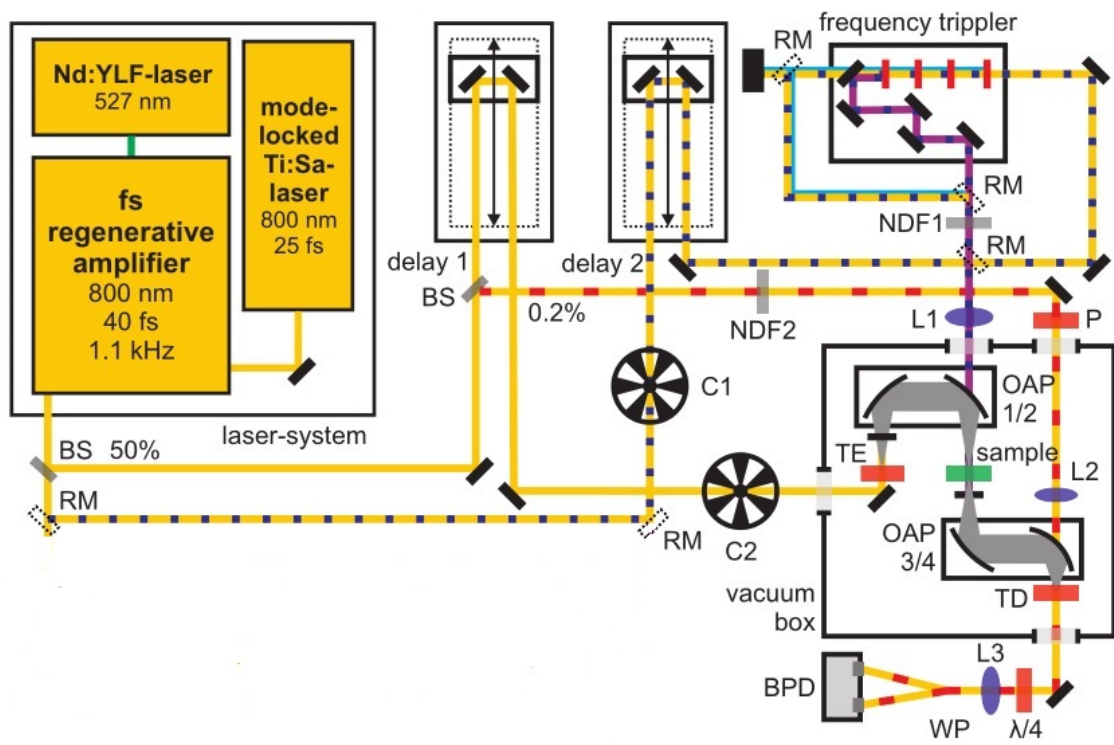


Figure 3.2: Schematic layout of the optical-pump-terahertz-probe setup. (NDF: neutral density filter, C: chopper, P: polariser, L: lens, TE: THz emitter, TD: THz detector, $\lambda/4$: quarter-wave plate, WP: wollaston prism, OAP: off-axis parabolic mirror, RM: removable mirror, BS: beam splitter, red-dashed beam: gate, blue-dotted beam: pump, solid beam: probe). Taken from Reference [9].

well-defined time-delay with respect to the pump pulse by using the above-mentioned motorized delay stages. Past the sample stage, remaining pump pulse components that have transmitted the sample get blocked by another PTFE beam blocker, while the transmitted THz pulse is collimated and focused onto the electro-optic detector crystal via another pair of off-axis parabolic mirrors, where it is measured by electro-optic sampling and the overlapping gate pulse. In order to guarantee an entirely linearly polarised gate pulse, it is sent through a polariser right before the detection, after which it propagates collinearly and simultaneously alongside the THz pulse into the detector crystal, again causing a polarisation change due to field-induced birefringence [156]. At this stage, a quarter-wave plate ($\lambda/4$) comes into action, re-converting the polarisation change into a nearly-circular polarised pulse, which the Wollaston Prism (WP) separates into horizontally and vertically polarised components, whose relative intensity is measured by a pair of biased p-i-n photodiodes.

Since the measured signals are relatively weak and yield a low signal-to-noise ratio, a double lock-in technique is applied to safely enhance the measured signals. For this purpose, the respective excitation beams are modulated onto a well-chosen carrier-frequency, which is accomplished by periodically blocking the excitation beams with the above-mentioned rotating chopper wheels employed in this setup. A lock-in amplifier then isolates the carrier frequency component in the output of the photodiodes, while a pair of dual-phase lock-ins eventually measures the change in THz transmission in two stages, relying on a back-to-back feed-in from the high carrier frequency modulated THz probe pulse and the 20 times lower carrier frequency signal of the optical pump pulse [9].

3.1.5 Data Analysis

Derivation of photoconductivity and charge-carrier mobility from change in THz electric field transmission.

Assuming the thickness of the perovskite film is smaller than the THz wavelength, the sheet photoconductivity ΔS of a thin film between two media of refractive indices n_a and n_b can be expressed as follows [165]:

$$\Delta S = -\epsilon_0 c (n_a + n_b) \frac{\Delta T}{T} \quad (3.1)$$

where the product $\epsilon_0 c$ denotes the invert of the vacuum impedance and $\frac{\Delta T}{T}$ the photo-induced change in THz electric field transmission over total transmission. As the experiment has been performed in an evacuated box under vacuum, the samples are surrounded by vacuum from one side ($n_a = 1$) and in direct contact with the z-cut quartz substrate from the other side ($n_b = 2.13$) through which the photoexcitation of the sample occurs.

The charge-carrier mobility μ can be calculated as follows:

$$\mu = \frac{\Delta S A_{eff}}{N e} \quad (3.2)$$

where ΔS is the sheet photoconductivity of a thin film, e the elementary charge and N the number of photoexcited charge-carriers. A_{eff} is the effective area of overlap between the optical pump and THz probe pulse calculated as follows:

$$A_{eff} = \frac{\pi}{\ln(2)} (FWHM_{pump}^2 + FWHM_{probe}^2) \quad (3.3)$$

while the number of photoexcited charge-carriers N can be determined as follows:

$$N = \phi \frac{E \lambda}{h c} (1 - R_{pump}) (1 - T_{pump}) \quad (3.4)$$

where ϕ is the ratio of charge-carriers produced following photon absorption, also known as the photon-to-charge branching ratio, which is assumed to be unity. E , is the energy contained in an optical excitation pulse of wavelength λ . E is the energy contained in an optical excitation pulse of wavelength λ , R_{pump} the reflectivity of the sample at normal incidence of the excitation beam and T_{pump} denotes for the portion of the pump beam which is transmitted through the sample. As ϕ is declared unknown, an effective mobility $\mu_{\text{eff}} = \phi \mu$ directly obtainable from the experiments is defined:

$$\phi \mu = -\epsilon_0 c (n_a + n_b) \frac{A_{\text{eff}} h c}{E e \lambda (1 - R_{\text{pump}}) (1 - T_{\text{pump}})} \frac{\Delta T}{T} \quad (3.5)$$

The ascertained charge-carrier mobility contains contributions from both electrons and holes. Hence, the derived values for mobility represent the sum of electron and hole mobilities. As ϕ ranges between 0 and 1, the effective mobility describes a lower limit.

Global Fits to THz photoconductivity transients

The recombination dynamics of the free charge-carrier density $n(t)$ is determined by first, second and third order decay mechanisms evaluated in the following rate equation:

$$\frac{dn(t)}{dt} = -k_3 n^3 - k_2 n^2 - k_1 n \quad (3.6)$$

The experimentally observed quantity of photo-induced THz transmission change $x(t) = (\frac{\Delta T}{T})(t)$ is linearly related to the free charge-carrier density in the form of

$$n(t) = \phi C x(t) \quad (3.7)$$

where, $C = \frac{n_0}{x(0)}$ is the proportionality factor between the immediate THz response $x(0)$ and the initially absorbed photon density n_0 :

$$n_0 = \frac{E \lambda \alpha(\lambda)}{h c A_{eff}} (1 - R_{pump}) \quad (3.8)$$

which can be derived from pump beam parameters and the absorption coefficient α at an excitation wavelength of 400 nm. Substituting 3.7 into 3.6 brings about the following relation:

$$\begin{aligned} \frac{dn(t)}{dt} &= -C^2 \phi^2 k_3 x^3 - C \phi k_2 x^2 - k_1 x \\ &= -A_3 x^3 - A_2 x^2 - A_1 x \end{aligned} \quad (3.9)$$

with $A_i = C^{i-1} \phi^{i-1} k_i$. Taking a fluence dependent set of THz photoconductivity transients belonging to a particular film, numerical solutions are fitted simultaneously ('globally') to all transients. Therefore, there is only one globally optimized value for A_i applied to all fluences. Because a spatially varying charge density profile is to be expected, the fit routine also considers the exponential charge density profile created by the pump beam. The sample is divided into 30 equally thick slices and the decay function is computed for all of these individually.

Calculation of Charge-Carrier Diffusion Length

The diffusion length is a measure for the average distance a photogenerated charge-carrier can move between generation and recombination. In order to further investigate the effects of charge-carrier mobility and recombination rate changes, the diffusion lengths L_D were calculated as follows:

$$L_D(n) = \sqrt{\frac{D}{R_{total}(n)}} \quad (3.10)$$

where the total recombination rate R_{total} is determined by the charge-carrier density and the recombination rate constants (k_1 , k_2 , and k_3) of the individual recombination processes:

$$R_{total} = -\frac{1}{n} \frac{dn}{dt} = n^2 k_3 + n k_2 + k_1 \quad (3.11)$$

Here, the diffusion constant D is the product of the mobility μ , Boltzmann constant k_B , and temperature T divided by the elementary charge e :

$$D = \frac{\mu k_B T}{e} \quad (3.12)$$

3.2 Photoluminescence Spectroscopy

Assuming a simplistic model of a two-state quantum system, the phenomenon of luminescence describes the radiative emission of photons caused by an electron making a discrete transition from an excited, higher energy state, to an equilibrium, lower energy state [166]. Since energy must be conserved, a semiconductor that emits photons must not be in equilibrium and therefore must have had excess energy injected into the sample from prior photoexcitation. The combination of photoexcitation and a subsequent luminescent dissipation of excess energy is the process which is typically termed as *photoluminescence (PL)*. The rates of radiative transitions are summarized by Einstein coefficient's of stimulated and spontaneous emissions, where the *Einstein A coefficient* is defined in terms of the total rate of spontaneous emission from the higher to the lower energy level [167]. In spectroscopy, photoluminescence has proven to be a valuable non-contact technique for the study of dynamic decay processes involving such characteristic energy level transitions. Above all, a time-resolved detection of the radiative decay discloses significant information on the charge-carrier lifetime of an excited state, while from steady-state measurements obtained emission spectra in this work are used to monitor the energy distribution and intensity of emitted photons as a function of wavelength.

3.2.1 Steady-State Photoluminescence

The intensity and type of PL depends on the material being studied and the laser wavelength used for excitation. Thus, by recording steady-state PL spectra of compositionally varying perovskite systems, their bandgap tunability in the visible spectrum can effectively be demonstrated. For PL-stability tests, Chapter 3.2.3 shows

a supplementary experimental setup measuring the behaviour of these spectra as a function of time under continuous light illumination.

Experiment:

Steady-State PL spectra were measured by photoexciting the sample material with 40 fs pulses generated by the 1.1 kHz repetition rate regenerative amplifier from the OPTP setup described in Chapter 3.1.4. As already mentioned, the wavelength of the optical excitation in the OPTP setup can be switched between 400 nm and 800 nm. However, for all perovskite systems investigated in this work the excitation wavelength was set at 400 nm. The sample is photoexcited in a dark, vacuum-sealed box and the large free-space PL light is collected by a collimating lens which feeds the PL into an attached optical fiber at an optimised angle (Figure 3.4). The light is then transported out of the vacuum chamber via a vacuum feedthrough that bridges over to another optical fiber patch cable, finally reading the signal into a portable USB-connected UV-Vis-NIR spectrometer (Ocean Optics USB 2000+). A back panel USB connection of the spectrometer is further used to establish contact with a PC, where the spectrum graphs of the detected PL can be monitored and saved by means of a corresponding processing software (SpectraSuite).

3.2.2 Time-Correlated Single Photon Counting

Carrying out time-resolved PL spectroscopy in the time domain requires the recording of time dependent intensity profiles of PL light emitted upon photoexcitation. Major obstacles for recording the intensity profile can impede the adequate capture of the relatively fast nanosecond-range decay transient and requires the setup of correspondingly fast-response and light-sensitive detectors. Among others, the manifold

challenges include light emission that is too weak to create a sufficiently strong analog voltage output, transient recording detectors with high rise and fall times, thus limiting the time-resolution, a problem which is technically even further complicated by very short measurement intervals caused by high repetition rates of pulsed laser light in the MHz range. One way to partly overcome such restraints is by using the *time-correlated single photon counting (TCSPC)* method. Here, the periodic optical excitation extends the signal detection over multiple cycles of emission, which enables the reconstruction of the luminescent decay profile from the multitude of single photon events collected over the cycles [168]. The reconstruction of the decay profile is only successful if the probability to detect more than one photon in one photoexcitation is kept low by using a sufficiently reduced excitation fluence and a high repetition rate [169]. This can be achieved by attenuating the PL down to one photon detection per approximately 1000 cycles. After many cycles, a histogram of the arrival times of the photons is built and translated into a PL decay profile, which is of exponential nature at low excitation fluences. The schematic working mechanism of the TCSPC method is displayed in Figure 3.3.

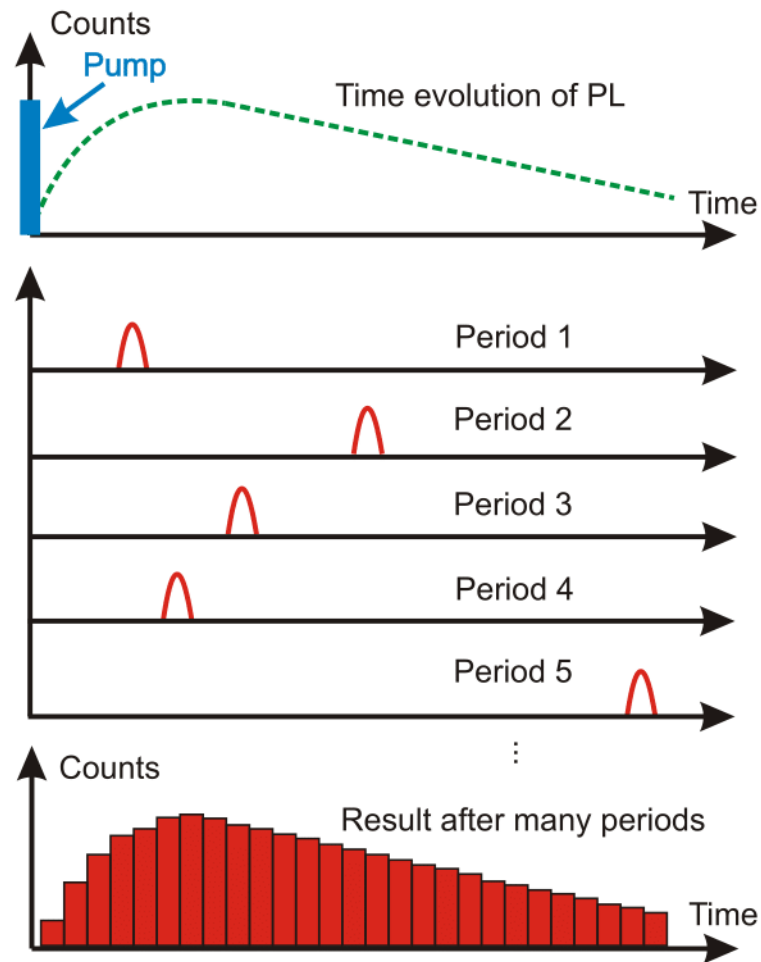


Figure 3.3: Schematic representation of the TCSPC technique. (a) shows the time evolution of the PL of one signal period after photoexcitation, (b) reveals how during each signal period the PL is reduced to at most a single photon, while (c) illustrates a histogram of the photon arrival times after many photoexcitation cycles, which is required for reconstructing the original PL signal and its underlying decay dynamics. Taken from Reference [170].

Experiment:

A diode laser (PicoQuant LDH-D-C-405M) with a pulse width below 200 ps and a fixed output wavelength of 400 nm is used to excite a sample sealed in a vacuum cell. The pulse repetition rate, with tunable frequencies up to 80 MHz, can be varied depending on the required observation window on the time scale. This becomes particularly important for slower recombination processes which need correspondingly longer time scales. The excitation energy from the described laser source is attenuated down to sufficiently low excitation fluences by using a discrete neutral-density filter wheel right after the output. The attenuated laser pulse excites the sample material synchronously with an internal triggering pulse on the detection unit to mark the start of the measurement period. Subsequently, the excitation pulse causes electrons to radiatively recombine and emit photons. A long-pass filter blocks any excitation light scattered from the sample, whereas the emitted light traverses a system of PL collection optics comprising of optical lenses, a variable aperture and linear polarizer. Finally, the optical path of the PL changes course for a diffraction-grating monochromator (Princeton Instruments, SP-2558) which enables a spectral selection of the peak emission wavelength, ideally determined from previously taken steady-state PL spectra. This signal is finally detected in a p-i-n diode.

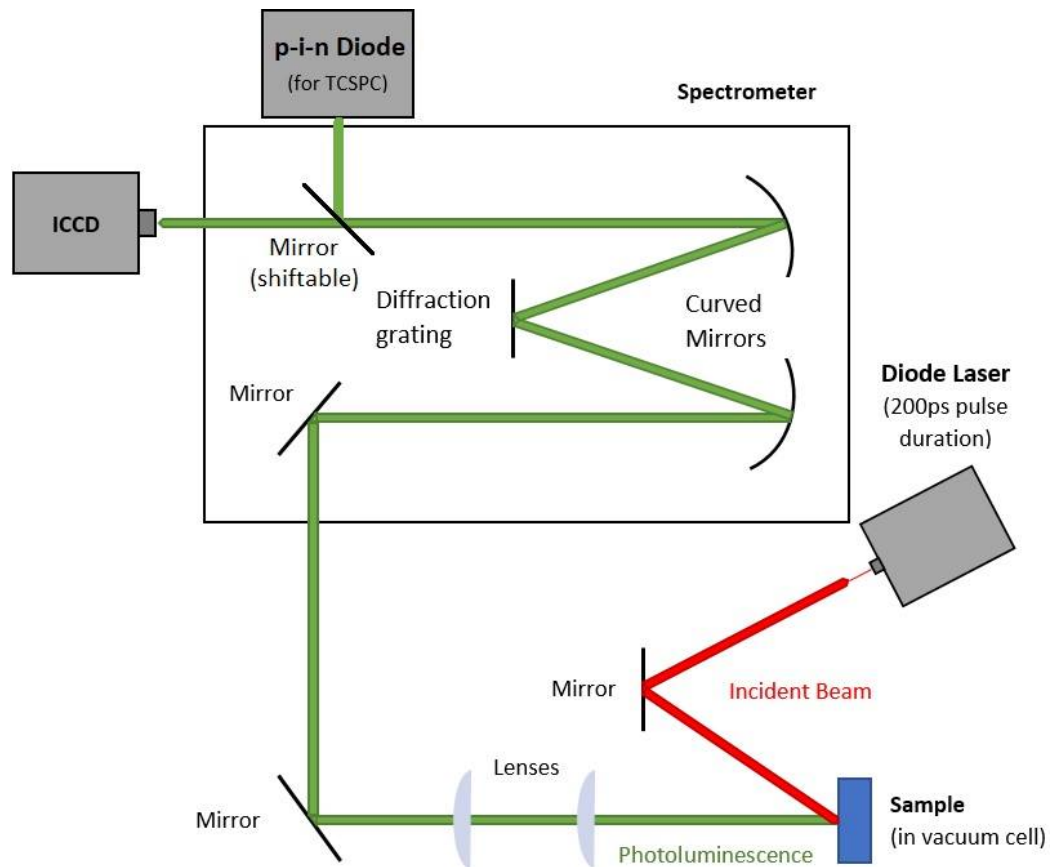


Figure 3.4: Schematic layout of the TCSPC experimental setup. The sample is excited by a pulsed diode laser and attenuated by a discrete neutral-density filter wheel to lower the fluence. Upon excitation, the sample creates a photoluminescence output, which is collected in a system of optics composed of (achromatic doublet) lenses, a variable aperture, longpass-filter and a linear polarizer. After passing through a diffraction-grating monochromator, the signal is detected by either a p-i-n diode for TCSPC measurements or an intensified-CCD detection unit if time-dependent PL spectra for PL-stability experiments are acquired.

3.2.3 Time-dependent Photoluminescence Stability

One key aspect of mixed-halide perovskite materials research is concerned with the spectral stability of the PL as a function of time under constant light illumination. To achieve meaningful results in this regard, a successive capture of steady-state PL spectra with high temporal resolution is pivotal for observing potential spectral shifts and associated changes of luminescence intensity and average energy of emitted photons. The basic design of the experimental setup used here is the same as for the TCSPC system discussed above (Chapter 3.2.2) except for changes in the triggering mechanism and the PL detection unit. An external waveform generator (Agilent 33500B) triggers both the excitation laser and the iCCD detection unit at a pulse frequency of 1 MHz. A PI-MAX4 iCCD gated imaging spectroscopy camera detects the signal and is capable of capturing PL emission with very high sensitivity and fast frame rates while the sample is exposed to either pulsed or continuous-wave laser light. If need be, another set of neutral-density filters can be applied to further attenuate the PL emission in order to prevent a potentially harmful saturation of the detector.

3.2.4 Data Analysis

Time-resolved Photoluminescence - TCSPC:

TCSPC measurements were undertaken at very low excitation fluences where higher order recombination processes are assumed to be negligible. Ideally, monomolecular recombination rates k_1 were extracted from stretched exponential fits to the tails of the low-fluence PL decay traces. The stretched exponential function, also known as Kohlrausch-function (Equation 3.13), is an ‘upgrade’ of the monoexponential decay function in the sense that it incorporates additional parameters such as the stretching

exponent β ($0 < \beta < 1$), which is used to calculate the average lifetime $\langle \tau \rangle$ (equation 3.14) instead of the characteristic lifetime τ :

$$f(t) = a \exp^{(-t/\tau)^\beta} \quad (3.13)$$

$$\langle \tau \rangle = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (3.14)$$

with $\Gamma(\frac{1}{\beta})$ being the the evaluation of the Gamma-function at $\frac{1}{\beta}$:

$$\Gamma\left(\frac{1}{\beta}\right) = \int_0^\infty x^{\frac{1-\beta}{\beta}} e^{-x} dx \quad (3.15)$$

Compared to simple monoexponential fits, calculating the average lifetime $\langle \tau \rangle$ takes into account the underlying heterogeneity resulting from a distribution of local monomolecular recombination rates k_1 . Values reflecting such monomolecular, charge-carrier density independent decay dynamics are represented in this work as lifetime $\langle \tau \rangle$ or its inverse value k_1 . It should be noted that the exact value derived for k_1 generally has little effect on the higher-order charge-carrier recombination parameters (k_2 & k_3) extracted from terahertz photoconductivity measurements because these are conducted at high charge-carrier density over a temporally much shorter window of 2.5 ns during which monomolecular decay is insufficiently active. While curves were acquired at lowest possible fluences and acquired reasonably quickly, photo-induced segregation may influence the PL traces creating additional error in the extracted monomolecular recombination rates k_1 .

Time-dependent Photoluminescence-Stability

The spectral shifts and changes in PL intensity of mixed-halide perovskites under light illumination are best described by the average photon energy of emitted photons, $\langle E \rangle$. This is the mean value of all photons emitted from a given PL spectra and provides a quantitative estimate of the effective wavelength in the spectral distribution of the PL emission.

First, the spectrum of the emitted PL is divided into small evenly spaced wavelength intervals. To calculate $\langle E \rangle$, the PL Intensity at each interpolated wavelength is divided by the corresponding photon energy, $I/\hbar\omega$, and the integral of the PL emission $E(\lambda)$ can be calculated from a PL spectra at a given time after illumination. This value is divided by the total photon flux density $\Phi(\lambda)$ which basically yields a number proportional to the number of all photons emitted in this process [171].

$$\langle E \rangle = \frac{\int_a^b E(\lambda) d\lambda}{\int_a^b \Phi(\lambda) d\lambda} \quad (3.16)$$

Alternatively, the average photon energy can also be expressed as follows [172]:

$$\langle E \rangle = hc(q\lambda_{eff})^{-1} \quad (3.17)$$

where λ_{eff} corresponds to:

$$\lambda_{eff} = \frac{\int_a^b \lambda E(\lambda) d\lambda}{\int_a^b E(\lambda) d\lambda} \quad (3.18)$$

with λ_{eff} being the effective wavelength, c , the speed of light in vacuum, and, h , the Planck constant.

Chapter 4

Charge-Carrier Dynamics and Stability of Formamidinium Lead Mixed-Halide Perovskites

A distinct benefit of organic-inorganic perovskite materials (e.g., over silicon) is that their bandgap can be tuned relatively easily with chemical composition, allowing attractive coloration and multijunction or tandem solar cell designs. For example, changing the metal cation at the B-site from Pb^{2+} to the less toxic Sn^{2+} to form MASnI_3 shifts the optical bandgap from 1.55 to 1.3 eV into the range of the ‘ideal’ single-junction solar cell bandgap between 1.1 and 1.4 eV [173, 174]. However, stability issues arising from the oxidation of tin have so far prevented widespread use. Alternatively, tuning the size of the A-site cation has been proven to change optical and electronic properties of the perovskite and to significantly influence solar cell performance [18]. Replacing MA in MAPbI_3 by the larger cation FA was found to decrease the bandgap from 1.57 to 1.48 eV [8, 41, 42], yield long PL lifetimes, high PCEs [18], and lower recombination and device hysteresis [175]. High PCEs in the order of 20% have been reported for solar cells based on FAPbI_3 [39, 50, 176] making this an attractive system to explore. In addition, the gradual replacement of the MA cation by FA through the film was shown to create a mixed-cation-lead-iodide OMHP allowing for energetic gradients [10]. However, mixing of the halide component in the perovskite offers the finest tuning of the optical properties of the perovskite

film. Here, the mixed organic lead bromide-iodide system has recently gained strong interest for application in OMHP solar cells [18, 37]. By changing the ratio between bromide and iodide (at the X-site anion), the bandgap can be tailored between 1.55 eV (MAPbI_3) and 2.3 eV (MAPbBr_3), which results in the coverage of much of the visible spectrum and paves the way for the development of tandem solar cells [37]. In addition to $\text{MAPb}(\text{Br}_x\text{I}_{(1-x)})_3$, its FA relative $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ has been explored [18]. Most fractional mixtures of $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ were found to be crystalline, with the exception of the region between $x = 0.3$ and $x = 0.5$ where the crystal structure changed, resulting in an amorphous region [18, 125]. A number of studies exploring the characteristics of solar cells based on the MAPbI_3 and MAPbBr_3 material system have been performed [177]. However, given the importance of this heterogeneous material system, little is known about the dynamics of photoexcited charge-carriers and their mobilities as a function of bromide-iodide content. A deeper understanding of these properties is therefore essential for further improvement of photovoltaic devices based on these highly tunable materials.

Here a key analysis of the charge-carrier dynamics including recombination rate constants and mobilities across the range of compositions in the mixed-halide lead perovskite system $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ is presented. The bimolecular and Auger recombination rate constants directly correlate with the Br-I fraction and are insensitive to phase stability. With an increasing Br-I ratio, charge recombination rate constants increase by up to an order of magnitude, with bimolecular recombination however remaining significantly below the Langevin limit. Because of their lack of correlation with material morphology, it is proposed that these are intrinsic charge recombination mechanisms that are directly linked with changes in electronic structure induced, e.g., by modifications of the frontier orbitals upon halide substitution. Charge-carrier mobilities, on the other hand, exhibit a strong correlation with phase disorder. For

the trihalide systems, FAPbBr₃ and FAPbI₃, establish effective charge-carrier mobilities of $(14 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $(27 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are established. For the intermediate mixed-halide materials, charge-carrier mobilities fall in correlation with increasing phase disorder, as evidenced by a rise in energetic broadening and trap-induced recombination mechanisms.

4.1 Sample Preparation

4.1.1 Perovskite Precursor Synthesis

Formamidinium iodide (FAI) and formamidinium bromide (FABr) were synthesised by dissolving formamidinium acetate powder in a 1.5 time molar excess of 57% w/w hydroiodic acid (for FAI) or 48% w/w hydrobromic acid (for FABr). After addition of acid, the solution was left stirring for 10 minutes at 50°C. Upon drying at 100°C C, a yellow-white powder was formed. This was then washed with diethyl ether and recrystallised with ethanol to form white needle-like crystals. Before use, it was dried overnight in a vacuum oven. To form FAPbI₃ and FAPbBr₃ precursor solutions, FAI and PbI₂ or FABr and PbBr₂ were dissolved in anhydrous N,N-dimethylformamide (DMF) in a 1:1 molar ratio at 0.55 M of each reagent to give a 0.55 M perovskite precursor solution. All precursor solutions were prepared by Dr Giles Eperon.

4.1.2 Film Fabrication

Immediately prior to film formation, small amounts of acid were added to the stock precursor solutions to enhance the solubility of the precursors and allow smooth and uniform film formation. To 1 ml of the 0.55 M FAPbI₃ precursor solution, 38 µl of

hydroiodic acid (57% w/w) was added, and 32 μ l of hydrobromic acid (48% w/w) was added to 1 ml of the 0.55 M FAPbBr₃ precursor solution. To form the FAPb(Br_xI_(1-x))₃ perovskite precursors, mixtures were made of the FAPbI₃ and FAPbBr₃ solutions in the required ratios after the addition of acid. Films were then spin-coated on warm (85°C) z-cut quartz substrates at 2000 rpm in a nitrogen-filled glovebox and subsequently annealed in air at 170°C for 10 minutes. This procedure gave very uniform pinhole-free layers of FAPb(Br_xI_(1-x))₃ with a thickness of $\approx$ 300 - 400 nm. All samples were prepared by Dr Giles Eperon.

4.2 Results and Discussion

4.2.1 Structural and Optical Characterisation

Figure 4.1 displays steady-state PL spectra for thin films of FAPb(Br_xI_(1-x))₃ with varying bromide content between $x = 0$ (100% iodide) and $x = 1$ (100% bromide). In agreement with previous reports [35], the PL peak energy is found to tune continuously from 2.26 eV for FAPbBr₃ to 1.50 eV for FAPbI₃. Theoretical calculations show that the red shift upon moving from Br to I derives from the associated decrease of the electronegativity of the halogen atom [178]. Exchanging Br with I changes the nature of the halide frontier orbital contribution to the valence band from 4p to 5p, which decreases the bandgap energy [111, 179]. The observed PL peak positions are consistent with the absorption onsets seen in absorbance spectra of the examined FAPb(Br_xI_(1-x))₃ films (Figure 4.2) confirming that the PL arises primarily from band-edge emission rather than from minority phases or trap states.

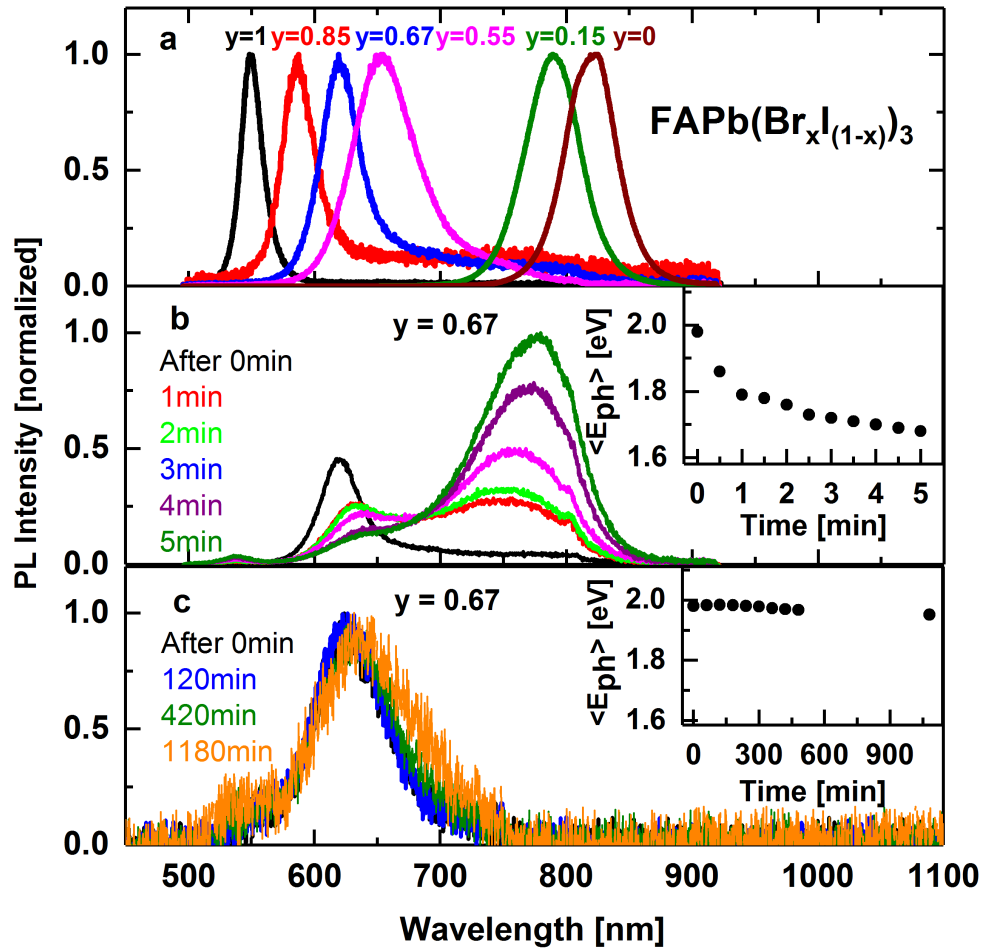


Figure 4.1: a) Steady-state PL spectra of thin films of $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ perovskite with varying halide composition x , recorded immediately following excitation at 400 nm at a fluence of $0.1 \mu\text{J cm}^{-2}$ (7.2 W cm^{-2}) under vacuum. The PL spectra have been normalised to the peak emission. b) PL spectra of a $\text{FAPb}(\text{Br}_{0.67}\text{I}_{0.33})_3$ film over the course of 5 minutes of continuous illumination following excitation at 400 nm with an intensity of 7.2 W cm^{-2} (fluence of $0.1 \mu\text{J cm}^{-2}$, pulse duration 100 fs, repetition rate 80 MHz). Inset: Change of average photon energy $\langle E_{\text{ph}} \rangle$ as a function of illumination time. c) In situ PL spectra for a $\text{FAPb}(\text{Br}_{0.67}\text{I}_{0.33})_3$ film over the course of 1180 minutes of continuous illumination following excitation at 400 nm with an intensity of 15 mW cm^{-2} (fluence of $13.5 \mu\text{J cm}^{-2}$, pulse duration 40 fs, repetition rate 1.1 kHz). Spectra were collected in situ with a fiber-optic collection system under experimental conditions matching those used for acquiring time-resolved THz photoconductivity data shown in Figure 4.5. PL spectra have been normalised to the peak emission intensity. Inset: Change of the average photon energy $\langle E_{\text{ph}} \rangle$ as a function of time.

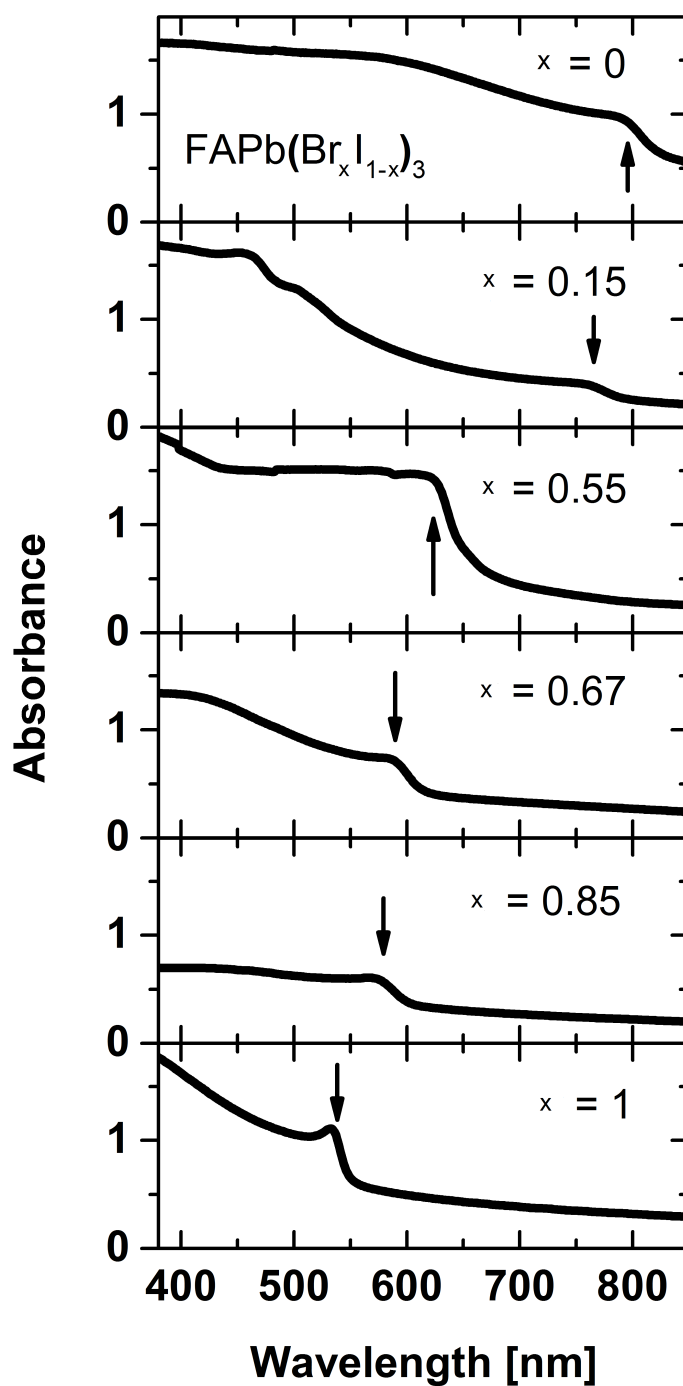


Figure 4.2: UV-VIS absorbance spectra of FAPb(Br_xI_(1-x))₃ films with varying halide composition. Vertical arrows indicate the absorption onsets. The spectra were recorded using a PerkinElmer Lambda 1050 UV/Vis/NIR spectrometer.

For $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ films with bromide content in the region $0.3 < x < 0.5$, the material quality appears significantly lowered, as apparent from the absence of significant PL emission and X-ray diffraction (XRD) data (Figure 4.3). While outside of this region, XRD shows sharp peaks arising from crystalline perovskite [18], the lack of such features in the intermediate region ($0.3 < x < 0.5$) suggests that the material becomes amorphous here, with amorphous implying that the crystalline order is on too short a length scale to be detectable in XRD data. Such structural disorder can be understood in the context of a crystal structure change: while FAPbI_3 adopts the trigonal structure [8, 50], FAPbBr_3 is cubic at room temperature [18]. Variation of bromide content for this system has been shown to lead to a monotonic change in pseudocubic lattice parameter determined from XRD, apart from the transition region of $0.3 < x < 0.5$ between which the structure transfers from cubic to tetragonal and no well-defined crystal structure can be formed [18]. In subsequent analysis, this region is therefore referred to as the amorphous region.

In previous work, a reversible light-induced transformation of PL spectra for mixed bromide-iodide perovskites has been reported, which raised concerns regarding the photo-stability of these mixed-halide materials [93]. Under constant illumination, bromide-rich $\text{MAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ perovskite films were found to exhibit a new dominant peak at around 740 nm, i.e., red-shifted toward the emission spectrum of MAPbI_3 [93]. It was proposed that photoexcitation may cause halide segregation into two crystalline phases: an iodide-rich minority domain and a bromide-rich majority domain [93]. This instability could be substantially detrimental for photovoltaic performance in solar cell devices since the expectation would be that the open-circuit voltage may then become limited by the energy of the lower bandgap phases. By contrast, other studies of PL emission from mixed-halide perovskite systems have not reported such light-induced shifts [18, 125]. Here, it is found that the intensity of the laser excitation spot plays a major role in producing these shifts. Figure 4.1b shows the PL

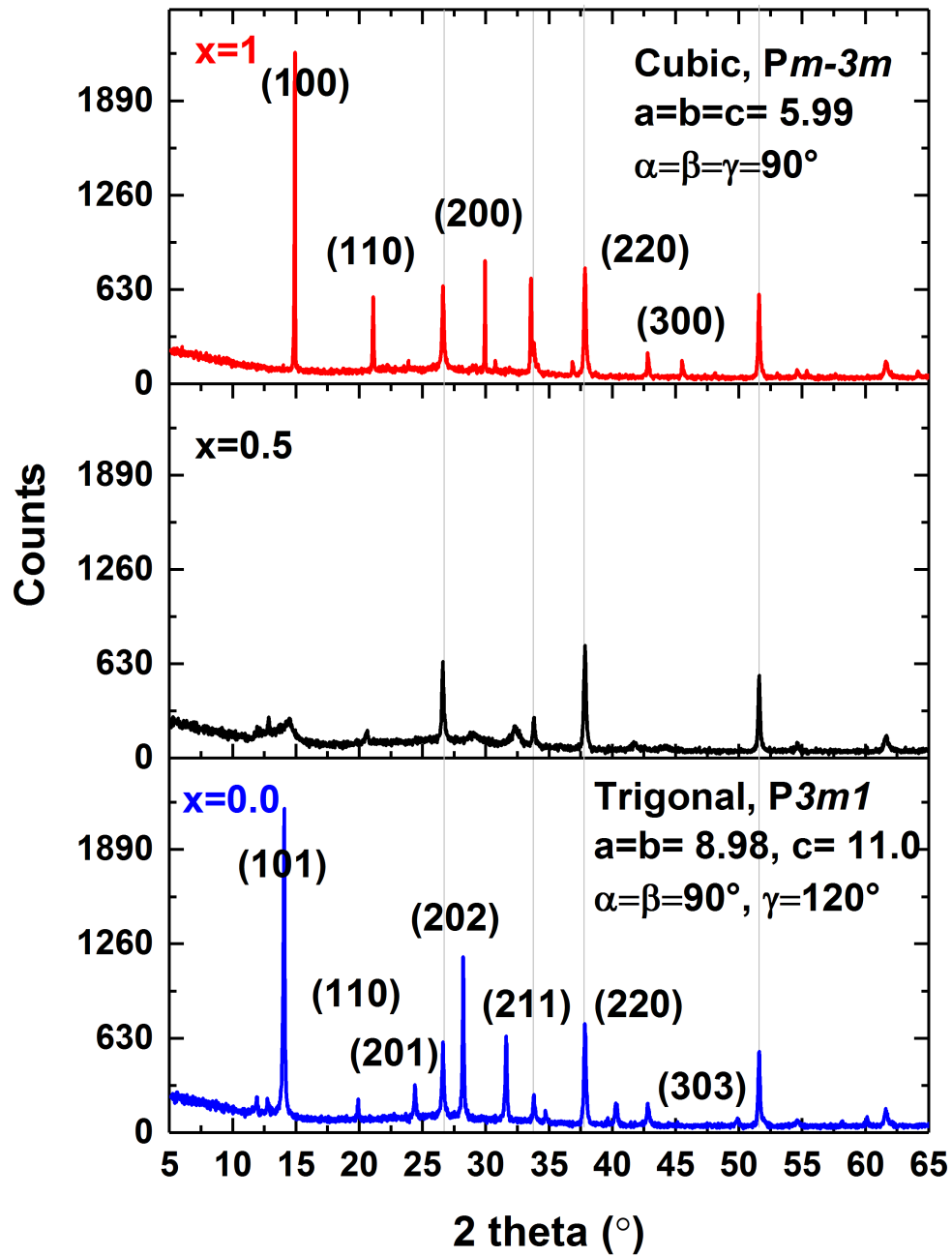


Figure 4.3: X-ray diffraction (XRD) spectra for FAPbBr₃ ($x = 1$), FAPb(Br_{0.5}I_{0.5})₃ ($x = 0.5$) and FAPbI₃ ($x = 0$) with peaks attributed to crystallographic diffraction planes in the perovskite indicated in brackets. The four peaks marked with grey lines arise from the FTO substrate that was present during the measurements.

emission of a $\text{FAPb}(\text{Br}_{0.67}\text{I}_{0.33})_3$ film (a composition on the bromide side of the phase instability) when recorded for laser excitation with an intensity of 7.2 W cm^{-2} following 5 minutes of continuous illumination. Indeed, here, the phenomenon of halide segregation-induced shifts is clearly corroborated. The original PL maximum at 620 nm almost completely shifts to a new dominant low-energy PL feature, which is recognizable at around 785 nm (1.58 eV). The luminescence intensity almost doubles with respect to the initial value, in accordance with higher PL emissivity of the iodide-rich phases. In addition, the enhancement of another small phase at around 540 nm (2.3 eV) is distinguishable. The inset of this figure presents the decrease of the average energy of emitted photons following pulsed laser excitation and shows a continuous decrease over time. Figure 4.1c, on the other hand, shows PL spectra for an identical $\text{FAPb}(\text{Br}_{0.67}\text{I}_{0.33})_3$ film under illumination at the same wavelength (400 nm) for 1180 min ($\approx 20 \text{ h}$) with laser intensity of 15 mW cm^{-2} . These were collected with an in situ (fiber-based) spectrometer under conditions identical to those employed in the time-resolved THz photoconductivity measurement described below. With an excitation intensity 500 times lower, negligible shifts in PL maxima and average photon energy are observed, and no new low-energy PL features emerge during continuous laser excitation over the time-scale of 20 h. While the primary aim of these measurements is to establish that the examined films do not phase-segregate or decompose during the time-resolved THz photoconductivity measurements described below, it should be noted that photovoltaic devices are typically tested under AM1.5 conditions ($1 \text{ kW m}^{-2} = 100 \text{ mW cm}^{-2}$), which is closer to the light intensity of 15 mW cm^{-2} for which no significant PL peak shifts are observed. These results may therefore explain why no instabilities in open-circuit voltages have so far been reported for mixed Br-I perovskite photovoltaic devices, and suggest that mixed-halide perovskites may yet be a usable route toward wider bandgap absorbers. They further highlight the need for more quantitative investigations into light-induced halide segregation in these mixed

systems (e.g., dependencies on light intensity, nonlinearities, heating, and morphology), which will ascertain the extent to which such effects are detrimental under photovoltaic device operating conditions.

4.2.2 Electronic Characterisation

With stability of materials under THz measurement conditions confirmed, the charge-carrier recombination dynamics in mixed-halide perovskites are analyzed. For this purpose, ultrafast optical pump - THz probe spectroscopy is utilised as a time-resolved, contactless conductivity probe, which has been used previously to study charge-carrier recombination rate constants for other perovskite materials [104, 105]. The question as to which optically excited species may couple to the THz probe pulse, either excitons or free charge-carriers, has been addressed several times in earlier reports [27, 119, 121, 122]. It can be noted that for MAPbI₃ the sole response to the THz conductivity probe has already been shown to be that of a free-charge carrier density, as inferred from the Drude shape of the conductivity spectra [104, 105]. Here, a highly similar Drude conductivity spectra for FAPbBr₃ is reported, which suggests that excitonic effects are negligible at room temperature for the mixed Br-I materials under investigation (Figure 4.4).

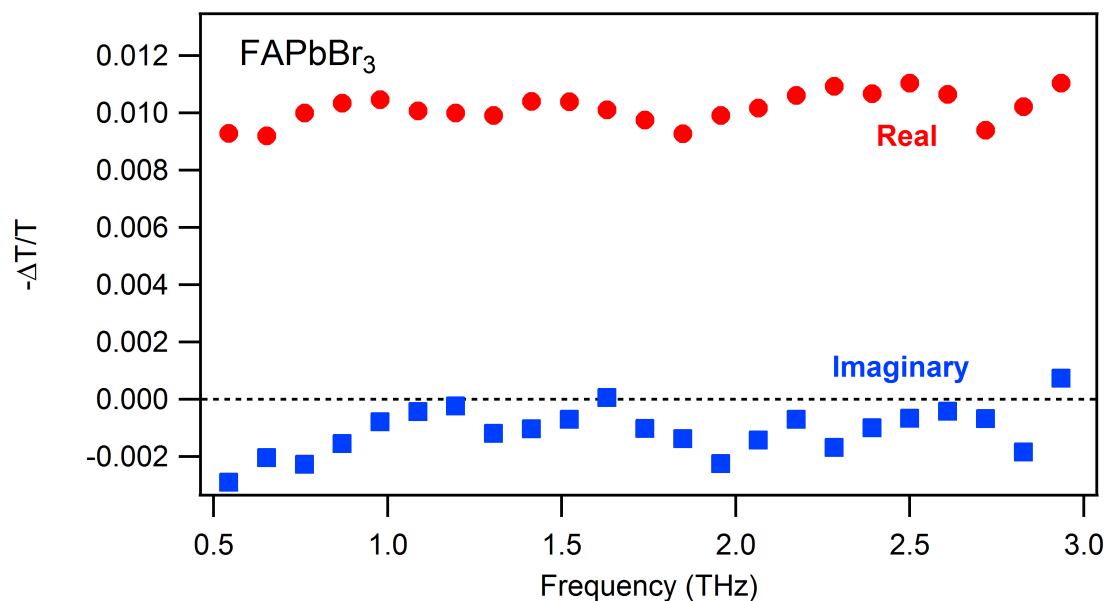


Figure 4.4: THz photoconductivity spectrum of FAPbBr₃ recorded at a pump-probe delay of 100 ps after excitation at 400 nm with a fluence of 65 $\mu\text{J cm}^{-2}$.

Figure 4.5 displays the THz photoconductivity transients of films with four different compositions of FAPb(Br_xI_(1-x))₃ after photoexcitation at 400 nm with excitation fluences ranging from 8 to 65 $\mu\text{J cm}^{-2}$. The transient conductivity originating from photoexcited charge-carriers is probed by a THz radiation pulse at a precise time-delay with regard to the pump pulse. The data shown in Figure 4.5 reveal a striking correlation between the photoconductivity decay dynamics and bromide content. When the bromide fraction x is increased from FAPbI₃ ($x = 0$, Figure 4.5a) to the lighter-halide perovskite, FAPbBr₃ ($x = 1$, Figure 4.5d), the initial decay components of the transients gradually become faster. This suggests that upon change from tri-iodide to the tri-bromide perovskite film, higher order recombination effects increase.

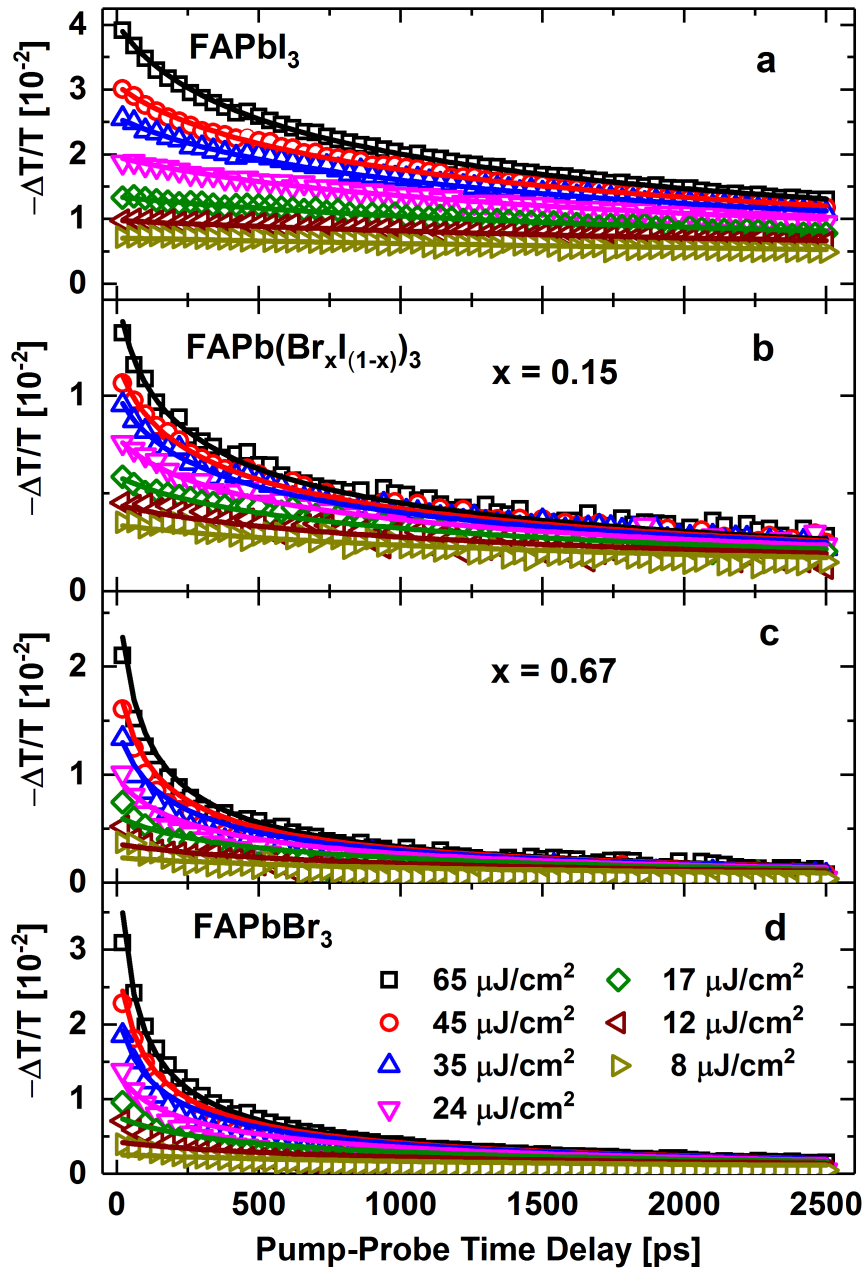


Figure 4.5: THz photoconductivity transients for thin films of $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ with a) $x = 0$, b) $x = 0.15$, c) $x = 0.67$, and d) $x = 1$, for excitation fluences between 8 and $65 \mu\text{J cm}^{-2}$ at 400 nm wavelength. The symbols represent data points, and the solid lines are fits as described in the text.

The decline in photoconductivity with increasing time after excitation is primarily the result of charge-carrier recombination, which is expected to depend on the charge carrier-density and therefore laser excitation fluence [104, 105]. For high charge-carrier densities, there will be an enhanced contribution from higher-order recombination mechanisms, such as second-order electron-hole (bimolecular) recombination as well as third-order Auger recombination, in which energy and momentum are transferred to a third charge-carrier [104]. Taking such effects into account, the associated recombination rate constants can be derived from fits to data of solutions to the following rate equation:

$$\frac{dn(t)}{dt} = -k_3n^3 - k_2n^2 - k_1n$$

where $n(t)$ is the free charge-carrier density, k_3 is the Auger recombination rate constant, k_2 is the bimolecular recombination rate constant, and k_1 is the monomolecular recombination rate, which may arise from charge trapping. Since the measured relative change in THz electric field transmission ($\frac{\Delta T}{T}$) is proportional to the photoinduced conductivity and thereby to the free charge-carrier density [180], fitting the above rate equation to the transients allows the extraction of recombination rate constants. Fitting was performed globally across all fluences, and the monomolecular decay rate constant k_1 was fixed to a value determined using time-resolved PL measurement at very low laser excitation densities for which higher-order recombination effects are negligible (Figure 4.6). However, it can be noted that since the monomolecular lifetime k_1^{-1} is significantly larger than the observation window of 2.5 ns for which THz data were taken, the exact value of k_1 has little influence on the fits.

Figure 4.7a,b demonstrates that both the bimolecular (k_2) and Auger recombination rates (k_3) increase monotonically with increasing bromide content and are an order of magnitude lower for FAPbI₃ compared to the lighter-halide FAPbBr₃. These results are notable because they suggest a clear link between these intrinsic electron-hole

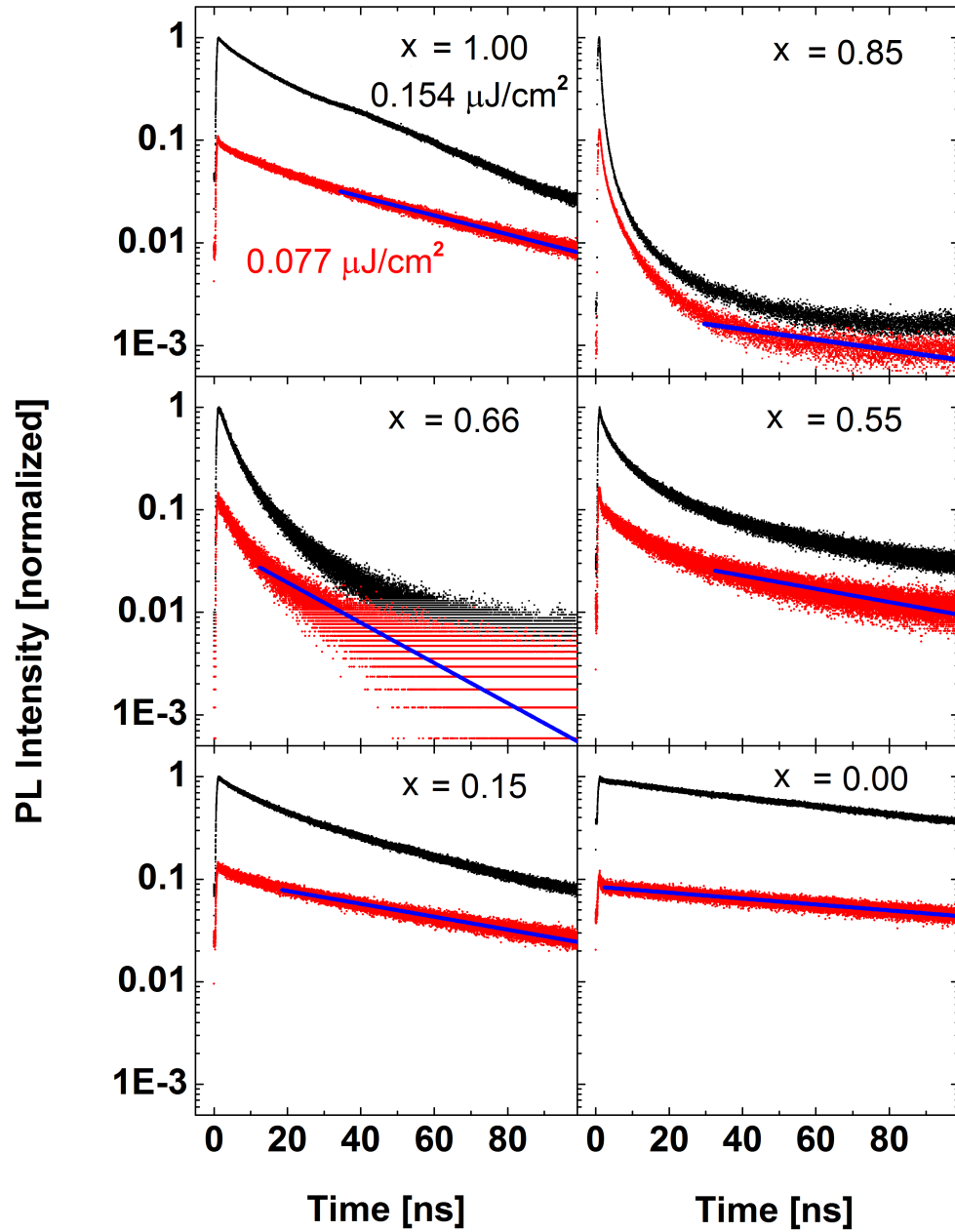


Figure 4.6: Time-resolved PL spectroscopy of $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ films following excitation at 400 nm with excitation fluences of $0.077 \mu\text{J cm}^{-2}$ (red trace) and $0.154 \mu\text{J cm}^{-2}$ (black trace). The laser intensity was at 7.77 W cm^{-2} for the lower fluence measurement.

recombination rate constants and the chemical composition and therefore electronic structure of the material. As discussed above, the material crystallinity is markedly lower toward the central region of $0.3 < x < 0.5$, however, the bimolecular and Auger recombination rates appear relatively insensitive to this, changing instead monotonically with x . As shown below, the situation is very different for the charge-carrier mobility and trap-related recombination rate, which are instead found to be strongly linked with material quality or crystallinity. However, bimolecular and Auger recombination do not show features near the central instability region, suggesting instead a correlation with fundamental electronic properties of the system. A gradual change in the intrinsic recombination parameters with bromide fraction may be expected for a number of reasons. First, the substitution of iodide with bromide changes the nature of the valence-band maximum, which has strong contributions from hybridizations of the atomic frontier p-orbitals of the halide [111] that may affect spontaneous bimolecular electron-hole recombination rates. In addition, the bimolecular recombination rates for hybrid metal-halide perovskites are suppressed well below the values predicted by Langevin theory, for which spatial segregation of electron-hole pairs across the metal-halide bond has been proposed as one possible origin [104, 105]. Here, similarly suppressed Langevin ratios across the whole $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ system are found. Changes in halide composition may affect such spatial segregation and in turn tune the bimolecular recombination rates. For Auger recombination, rate constants generally depend strongly on the electronic band structure of the semiconductor because of the need for overall momentum and energy conservation involving the many-body process [181]. For the $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ system, a gradually decreasing pseudocubic lattice parameter has been reported with increasing bromide fraction [18] in agreement with a continuous change in electronic band structure; however, the exact correlation between Auger recombination and crystal structure is likely to be complex. These investigations open up new possibilities for linking optoelectronic

properties of these promising materials with calculations that may eventually allow materials design from first principles.

Charge-carrier mobilities also play a significant role in the performance of photovoltaic devices, affecting charge extraction to electrodes. Effective charge-carrier mobilities $\varphi\mu$ for the mixed-halide $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ films are determined from the photoconductivity onset value at zero pump-probe delay and with knowledge of the initially absorbed photon density and other optical parameters. Although effective charge-carrier mobilities are derived as lower bounds of the actual mobility, it is assumed that the photon-to-free-charge conversion ratio φ is close to unity because of the observed Drude-like photoconductivity spectra, as discussed above.

Figure 4.7c displays the extracted charge-carrier mobility values as a function of bromide content. For FAPbI_3 ($x = 0$), a value of $(27 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is found, similar to values previously determined for solution-processed meso-superstructured MAPbI_3 films [105] and vapour-deposited solid $\text{MAPb}(\text{I}_x\text{Cl}_{(1-x)})_3$ films [104]. Interestingly, FAPbBr_3 ($x = 1$) also shows a remarkably high mobility value of $(14 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, only lower by a factor of 2 than that for the iodide-only material. All of the examined mixed-halide materials, however, exhibit charge-carrier mobilities below these two limits. Unlike the bimolecular and Auger recombination kinetics discussed above, the obtained charge mobilities exhibit a clear correlation with increasing electronic disorder. For the amorphous intermediate-region films ($0.3 < x < 0.5$), charge mobilities exhibit a significant drop decreasing down to $(2 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $x = 0.3$ and $(1 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $x = 0.4$ films. The full width at half maximum (FWHM) of the PL emission peaks from $\text{MAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ films has recently been shown to be a reliable measure for phase stability, correlating directly with the Urbach energy [125]. Figure 4.7d shows the FWHM extracted from the PL peaks shown in Figure 4.1 for the $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ films investigated here. The PL FWHM shows clear correlation with the extracted charge-carrier mobility values, providing a

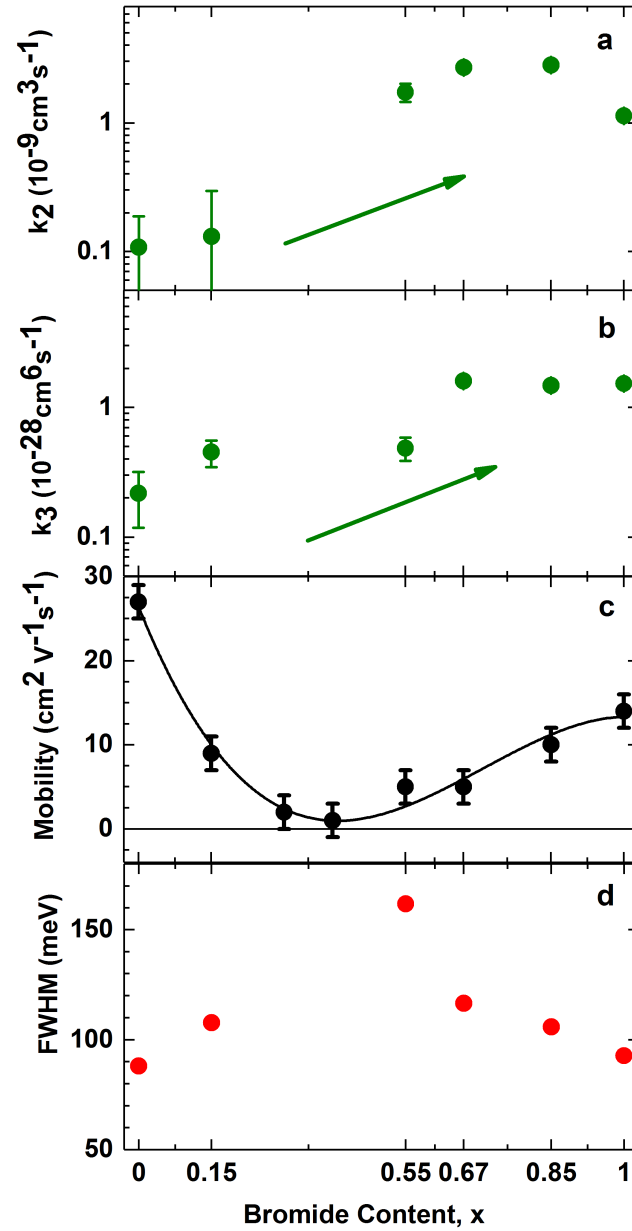


Figure 4.7: a) Bimolecular and b) Auger-recombination rate constants, k_2 and k_3 , for varying bromide content x in thin films of $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ perovskite. The constants were extracted from fits to THz photoconductivity transients; values are also listed in Figure 4.9. c) Effective charge-carrier mobilities of mixed-halide $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ perovskite films with varying bromide content. The solid line is a guide to the eye. d) Full width at half maximum (FWHM) of the PL emission peak versus bromide content.

direct link between the presence of disorder and a lowering in charge mobility. The neat tri-halide perovskite films display the lowest FWHM, in accordance with very low crystalline phase disorder and sharp band edges for these films [125]. In addition, it is found that the monomolecular recombination rate k_1 extracted from PL decay transients at low excitation fluence also exhibits a link with energetic disorder, although this may be superimposed on a general trend of increasing k_1 with increasing bromide content. Increasing disorder is likely to enhance such trap-induced monomolecular recombination, while changes in band structure may lead to modifications in relative trap energies, explaining the observed trends. Therefore, while single-halide lead perovskites show highly favorable charge-carrier lifetimes and transport, mixed-halide lead perovskites would benefit from newly devised routes toward manufacturing films with improved compositional homogeneity and therefore enhanced electronic order. Recent observations of strongly improved optoelectronic properties for MAPbX_3 ($X = \text{Br}, \text{I}$) single crystals grown by vapor-assisted crystallization demonstrate that decreasing disorder is a crucial aim for thin-film device applications [135].

From the measured charge-carrier recombination constants and mobilities, charge-carrier diffusion lengths (Equation 3.10, Chapter 3.1.5) as a function of charge-carrier density have been extracted (Figure 4.8), which are important figures of merit particularly for the use of these materials in planar-heterojunction device architectures. At a charge-carrier density of $n \approx 10^{15} \text{ cm}^{-3}$ which is typical during photovoltaic device operation, the charge carrier diffusion length calculated exceeds $1 \text{ }\mu\text{m}$ for the parameter space $0 < x < 0.15$ and $x = 1$, with the tri-iodide FAPbI_3 exhibiting the highest diffusion length of $3.1 \text{ }\mu\text{m}$ and the tri-bromide FAPbBr_3 a value of $1.3 \text{ }\mu\text{m}$, lowered by the lower charge-carrier mobility and higher charge-carrier recombination rates. For these materials, charge-carrier diffusion lengths clearly exceed the optical absorption depth (typically about a few hundred nm across the visible), in good agreement with the successful demonstration of efficient planar-heterojunction photovoltaic cells

for this range of x [18]. For the mixed-halide materials within the amorphous region, charge-carrier diffusion lengths are found in the range of 500 - 700 nm at $n \approx 10^{15} \text{ cm}^{-3}$, which is still respectable but may start to reduce charge-carrier collection efficiencies and maximum attainable open-circuit voltages in planar-heterojunction devices. However, the results suggest that only relatively modest improvements in disorder and trap density are required in order to make these Br-rich materials suitable for planar heterojunction device architectures.

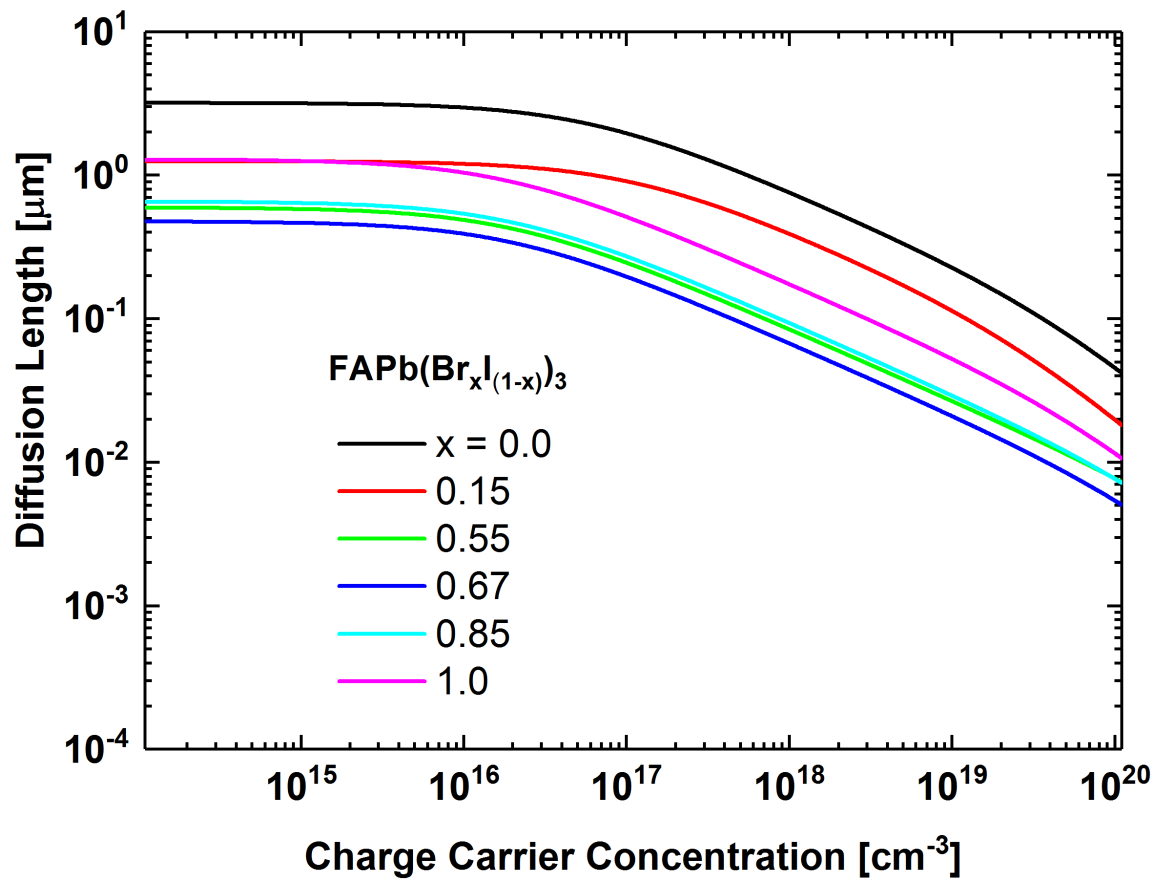


Figure 4.8: Charge-carrier diffusion lengths as a function of charge-carrier concentration for thin films of $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ with varying bromide content.

Furthermore, for elevated charge-carrier densities ($>10^{16} \text{ cm}^{-3}$), diffusion lengths gradually decline, as bi-molecular recombination starts to play a role. Such scenarios may be of relevance for solar concentrator applications or in a charge-accumulation regime. However, relative trends across the $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ system are maintained, because of the strong correlation between structural disorder and the charge-carrier mobility. In addition, it can be stressed that the charge-carrier diffusion lengths derived from such high-frequency THz measurements represent values that would be attributable to local domains with relatively unobstructed charge percolation pathways. Charge-carrier diffusion across a full film thickness may well encounter domain or crystal boundaries that act as additional barriers. Liang et al. have determined a charge-carrier diffusion length of $\approx 160 \text{ nm}$ for $\text{MAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ from diffusion induced PL quenching [182], while Kedem et al. found 360 nm for $\text{MAPbBr}_3(\text{Cl})$ using cross-sectional electron-beam-induced current measurements [183]. These values are lower than those established for matching bromide fractions here, which may be partly caused by differences in composition (MA instead of FA) or processing, but may also partly derive from the long-range charge diffusion methods employed by these groups.

4.2.3 Conclusions

In this study, key findings on the parameters governing charge-carrier dynamics and charge-carrier mobilities in a mixed-halide lead perovskite system were presented. Bimolecular and Auger recombination rate constants in $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ are found to strongly correlate with the relative Br content x , which suggests an inherent link with electronic structure and halide frontier orbital composition. For FAPbI_3 , both recombination rate constants, k_2 and k_3 , are found to be an order of magnitude lower compared to the lighter-halide FAPbBr_3 film. Such links may allow for predictive correlations to be established between desired charge-recombination properties and material composition. Unlike the recombination rate constants, charge-carrier mobilities across the mixed Br-I system exhibit a striking dependence on crystalline phase disorder. For FAPbBr_3 and FAPbI_3 films mobilities of $(14 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $(27 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ could be determined, respectively, whereas values for the mixed Br-I halide materials are lower than these two limits, and in comparison very low ($< 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for the amorphous region between $x = 0.3$ and $x = 0.5$. As a result, both iodide-rich and tri-bromide materials exhibit charge-carrier diffusion lengths exceeding $1 \text{ }\mu\text{m}$, however, this drops to values of the order of half a micrometer for the bromide-rich mixed systems. These findings suggest that making thermodynamically stable mixed-halide perovskites would significantly improve charge-carrier transport, allowing effective incorporation in planar-heterojunction tandem solar cell devices with high short-circuit currents, open-circuit voltages, and PCEs. In the following, all extracted key optoelectronic parameters from across the entire halide variation range are summarised (Figure 4.9):

Perovskite material composition	Charge-carrier decay constants			Effective Mobility	Langevin ratio	Charge-carrier diffusion length at $n=10^{15} \text{ cm}^{-3}$
	3 rd order	2 nd order	1 st order			
FAPb(Br _x I _{1-x}) ₃	$\phi^2 k_3$ ($10^{-28} \text{ cm}^6 \text{ s}^{-1}$)	ϕk_2 ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	k_1 (μs^{-1})	$\phi\mu$ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	$k_2/\mu : e/\epsilon_0$ (10^{-5})	L_d (μm)
x = 0.00	0.22±0.05	0.11±0.02	6.7±1	27	0.23	3.14
x = 0.15	0.45±0.11	0.13±0.05	14.5±3	9	0.79	1.25
x = 0.55	0.39±0.11	1.7±1.1	36±9	5	19.1	0.58
x = 0.67	1.6±0.3	2.7±0.8	45±9	5	30.0	0.47
x = 0.85	1.5±0.4	2.8±0.7	59±11	10	15.6	0.64
x = 1.00	1.5±0.4	1.1±0.3	21±3.0	14	4.52	1.26

Figure 4.9: *Column 1* presents the bromide content x of the FAPb(Br_xI_(1-x))₃ series. *Columns 2 and 3* show the third ($\phi^2 k_3$) and second (ϕk_2) order charge-carrier recombination rate constants extracted from THz photoconductivity transients. Errors displayed for $\phi^2 k_3$ and ϕk_2 were determined from the variation in output of the fitting routine for multiple datasets acquired for the same sample. Errors for k_1 arise mostly from slight deviations of the PL decay data from mono-exponential behaviour, which leads to a dependence of the fitting output on the time window over which data was fitted. *Column 4* presents monomolecular recombination rate constants k_1 extracted from monoexponential fits to the PL decay. *Column 5* lists the effective charge carrier mobility $\phi\mu$ determined from THz photoconductivity spectroscopy. *Column 6* compares the bimolecular recombination-rate-to-mobility ratio (k_2/μ) to that expected from Langevin theory (subject to factorization with an appropriate value of the dielectric function), and *Column 7* lists the diffusion lengths obtained for the low charge-carrier concentration regime ($n = 10^{15} \text{ cm}^{-3}$)

Chapter 5

Charge-Carrier Dynamics and Stability of Mixed-Cation Lead Mixed-Halide Perovskites

Numerous A-site cations, such as MA, FA and Cs, have so far been demonstrated to form excellent perovskite absorber layers for solar cells and in Figure 2.5 a whole string of other examples was presented. However, each of them bring along their own sets of advantages and difficulties: The all-inorganic CsPbI_3 indeed forms a photoactive black perovskite phase with a band gap of 1.73 eV [33]. For perovskites employing organic A-site cations like FA or MA, this is usually a region associated with energetic disorder. Nonetheless, this desired state for CsPbI_3 is only stable at high temperatures between 200°C and 300°C. In fact, the most stable phase at room temperature is a non-perovskite orthorhombic, so-called yellow phase. On the other hand, MA-based perovskites suffer from significant thermal instability because of the volatility of MA [71]. Hence, as matters stand, FA-based perovskites are considered a top contender for maintaining the best balance between thermal and structural stability [8, 10, 80, 109]. Although substituting MA with FA is reported to bring about thermally more stable perovskite films, the slightly increased optical band gap of FAPbX_3 has not triggered a corresponding increase in open-circuit voltage V_{OC} yet [18]. Additionally, tuning across the entire mixed-halide bromide-iodide range, a crystal phase transition is observed from trigonal to cubic structure. As discussed

in the previous chapter, near the transitional mid-bandgap region, all material compositions exhibit an insufficient degree of crystallisation, resulting in a seemingly amorphous phase with strongly increased energetic disorder and unexpectedly low absorption. Furthermore, the charge-carrier mobility in this region is substantially lowered, with only $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ compared to $>20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the tri-iodide perovskite. With respect to tandem-design applications, this is problematic given that this crystallisation problem has emerged precisely at bromide-iodide fractions ($0.3 < x < 0.5$) required to form the desired top-subcell bandgap of $\approx 1.7 - 1.8$ eV. Prone to photoinduced halide-segregation, bromide-rich films near this transition potentially see another limiting factor for the open-circuit voltage V_{OC} and thus PCE.

Consequently, in this chapter the challenging task of making a photostable FA-based perovskite with an ideal bandgap for tandem solar cells is addressed. For this, the FA cation is partially substituted with Cs which eliminates the instability caused by disordered crystal phases in the bromide-to-iodide compositional range, enabling a tunability of the band gap around 1.74 eV and a recovery of key optoelectronic parameters. In a planar heterojunction device, this material demonstrated a PCE of $>17\%$ and a stabilised power output of 16%.

5.1 Sample Preparation

5.1.1 Perovskite Precursor Synthesis

FAI and FABr were synthesised by dissolving formamidinium acetate powder in a 1.5x molar excess of 57% w/w hydroiodic acid (HI) and 48% w/w hydrobromic acid for FABr. Acid is added to the solution which is then left stirring for 10 minutes at 50°C. After Drying at 100°C for 2h, a yellow-white powder emerges, which is then then washed with diethyl ether. The powder is then dissolved in ethanol heated at 80°C which produces a supersaturated solution. The solution is stored in a cool place for overnight recrystallization upon which white needle-like crystals are formed. Ultimately, the powder is washed with diethyl ether for three times and dried overnight in a vacuum oven at 50°C. All precursor solutions were prepared by David P. McMeekin.

5.1.2 Perovskite Precursor Solution Mixture

For this work, two series of films ranging from neat I to neat Br were made; one series contains FA as the only cation and another with 83% FA and 17% Cs. In total, two different precursor solutions were made: FAPbI₃ and FAPbBr₃ for the FA series, and two additional precursor solutions for FA_{0.83}Cs_{0.17}PbI₃ and FA_{0.83}Cs_{0.17}PbBr₃, for the FA/Cs series. The solutions were dissolved in anhydrous N,N-dimethylformamide (DMF) and the following precursor salts were used to achieve a stoichiometric solution with the desired composition: FAI, FABr, CsI, CsBr, PbI₂, PbBr₂. 31.7 µl of 57% w/w hydroiodic acid (HI) and 18.8 µl of 48% w/w hydrobromic acid (HBr) were added to 1 ml of 0.55 M precursor solutions for both solutions. To form the optimised precursor solution for the FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ composition, FAI, CsI, PbBr₂ and PbI₂ were

dissolved in DMF to obtain a stoichiometric solution with the required composition and a molar concentration of 0.95M. 54.7 μl of HI and 27.3 μl of HBr were also added to 1 ml of 0.95 M precursor solutions. After adding acids, the solutions were stirred for 72 hours in a nitrogen atmosphere. All samples were spin-coated on z-cut quartz substrates by David P. McMeekin.

5.2 Results and Discussion

5.2.1 Structural and Optical Characterisation

Since previous reports have mentioned a bandgap change from 1.48 eV for FAPbI_3 to 1.73 eV for CsPbI_3 by simply interchanging the A-site cations [18], it can be assumed that mixing the inorganic Cs with organic FA or MA could result in just a slight widening of the band gap [77, 79]. The work reported in this chapter is based on the expectation that a partial substitution of FA for Cs could push the region of structural instability in the Br-to-I compositional range to higher energies, and in this way achieve a structurally stable mixed-halide perovskite with a band gap of $\approx 1.7 - 1.8$ eV. The photographs in Figure 5.1A show substrate-size thin films of single-cation $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ with the typically known yellowing of films towards the mid-bandgap region. In contrast, the mixed-cation lead mixed-halide $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ demonstrate no such yellowing, suggesting that crystal phase instabilities have effectively been held off due to the addition of Cs (Figure 5.1B). Astonishingly, not only the entire region of structural instability could be shifted to higher energies, but a continuous series of dark films emerged throughout the full compositional range. Ultraviolet-visible optical absorption measurements confirm this observation by revealing sharp optical band edges for all compositions of the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$

material (Figure 5.2), in stark contrast to $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$, which distinctly weakens in the intermediate range. XRD patterns measured for both series once more corroborate this finding: The material remains at a homogeneous phase across the entire tuning range with monotonic shifts of the (100) reflection occurring from $2\Theta \approx 14.2^\circ$ to 14.9° (Figure 5.3) corresponding to a shift of the cubic lattice constant from 6.306 to 5.955 Å arising from an increasing inclusion of the smaller halide, bromide, in the perovskite lattice system. On these accounts, it can be argued that for the mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ series, the structural phase transition and remnants of structural instability could be completely removed. For ensuing investigations, the mid-bandgap composition $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ will be examined, which has an optical band gap relevant for tandem solar cells designs (1.74 eV).

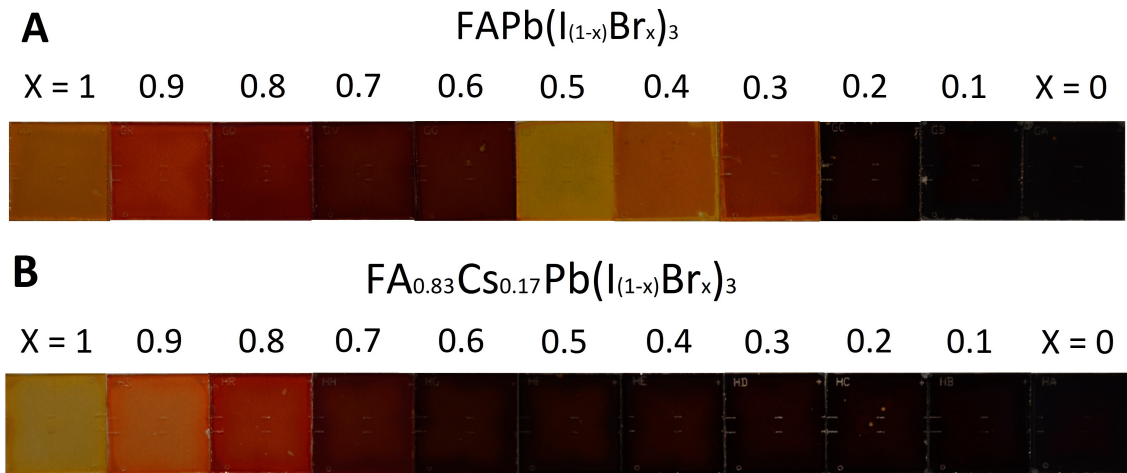


Figure 5.1: Photographs of perovskite films with varying halide composition ($0 < x < 1$) for single-cation $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ and mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ films. Samples prepared and photographs taken by David P. McMeekin.

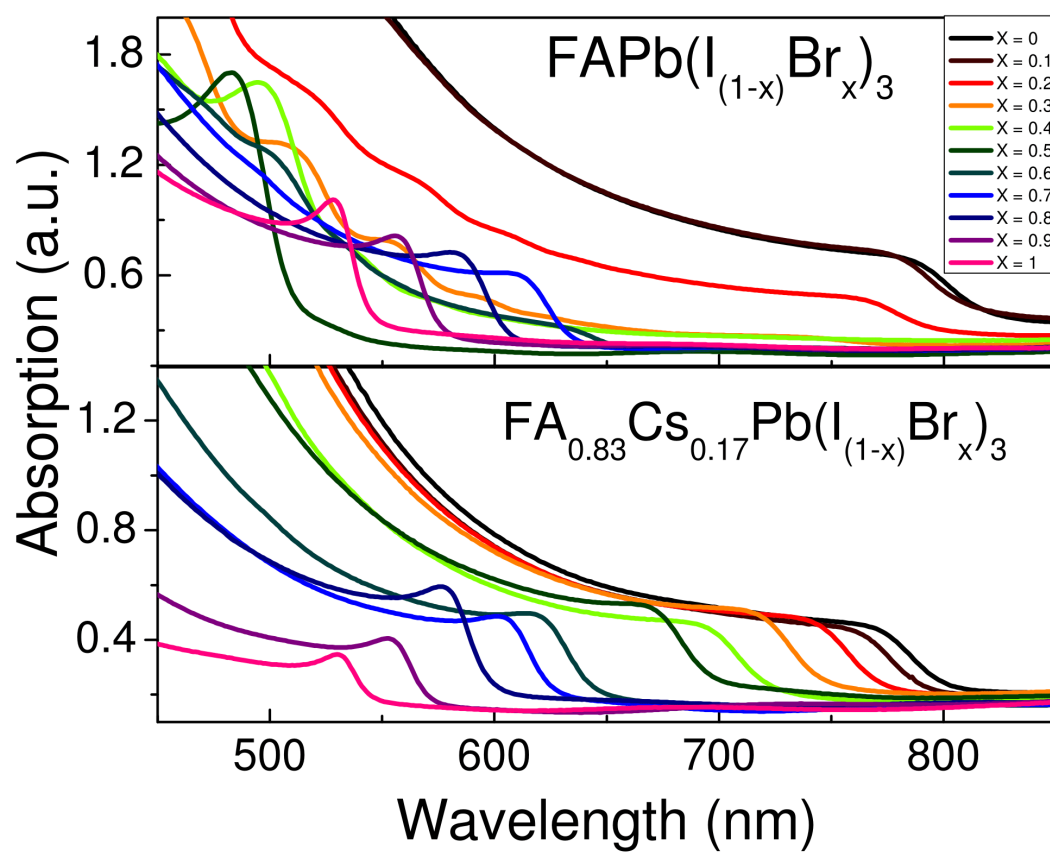


Figure 5.2: Ultraviolet-visible absorbance spectra of single-cation $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ and mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ films put in comparison. Data taken by David P. McMeekin.

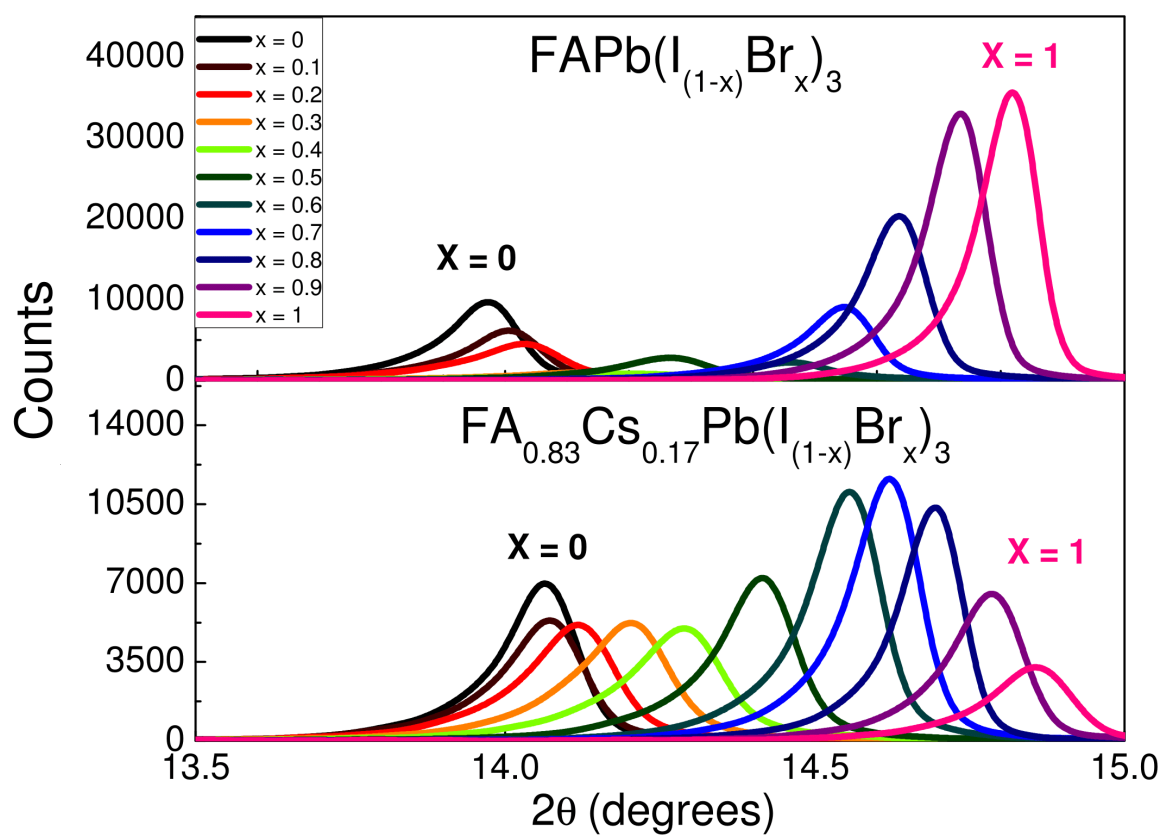


Figure 5.3: X-ray Diffraction spectra of single-cation $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ and $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$. Data taken by David P. McMeekin.

Apart from crystal phase instabilities, a major issue of mixed-halide perovskites is photoinduced halide-segregation upon which highly luminescent iodide-rich domains are formed at lower bandgaps substantially limiting the open-circuit voltage of the perovskite [93]. As reported in the previous chapter, such PL shifts upon continuous light illumination have also been observed for $\text{FAPb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites. This pattern of photo-instability is confirmed in Figure 5.4A where the PL of mixed-halide $\text{MAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskites is monitored under 3 mW cm^{-2} of continuous illumination at 550 nm, which induces PL peak shifts by 130 meV within a time period of 60 minutes. In contrast, the mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite does not exhibit any significant shift in PL emission under identical conditions, merely the PL intensity is observed to shoot up by orders of magnitude (Figure 5.4B).

This is a unique discovery which is probed into by further aggravating the conditions for the sample: In this case, another $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ sample is exposed to an intense monochromatic irradiance at 5 W cm^{-2} for 5 minutes, which corresponds to a more than three orders of magnitude higher laser intensity than the one used for the previous measurement. Strikingly, even in this case, the mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ shows no signs of significant redshift in PL emission suggesting that a highly improved structural stability is suppressing the photoinduced halide-segregation effect (Figure 5.5). Besides, the optical band gap and crystal lattice of the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ film remain stable under thermal stressing at 130°C , compared to those of single-cation $\text{MAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$, which normally degrade quickly under such conditions.

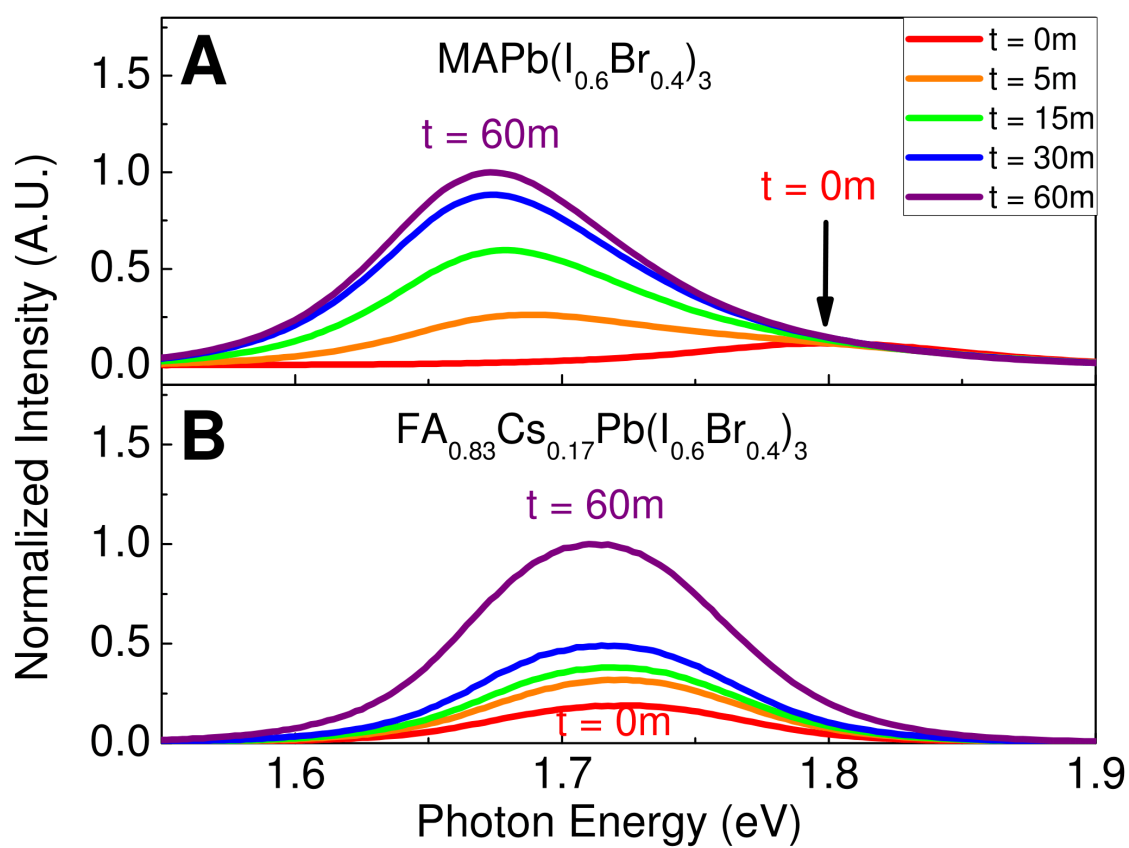


Figure 5.4: Normalised PL spectra of (A) single-cation $\text{MAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ and (B) mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin films, measured after 0, 5, 15, 30, and 60 minutes of continuous light illumination at 3 mW cm^{-2} , taken by David P. McMeekin.

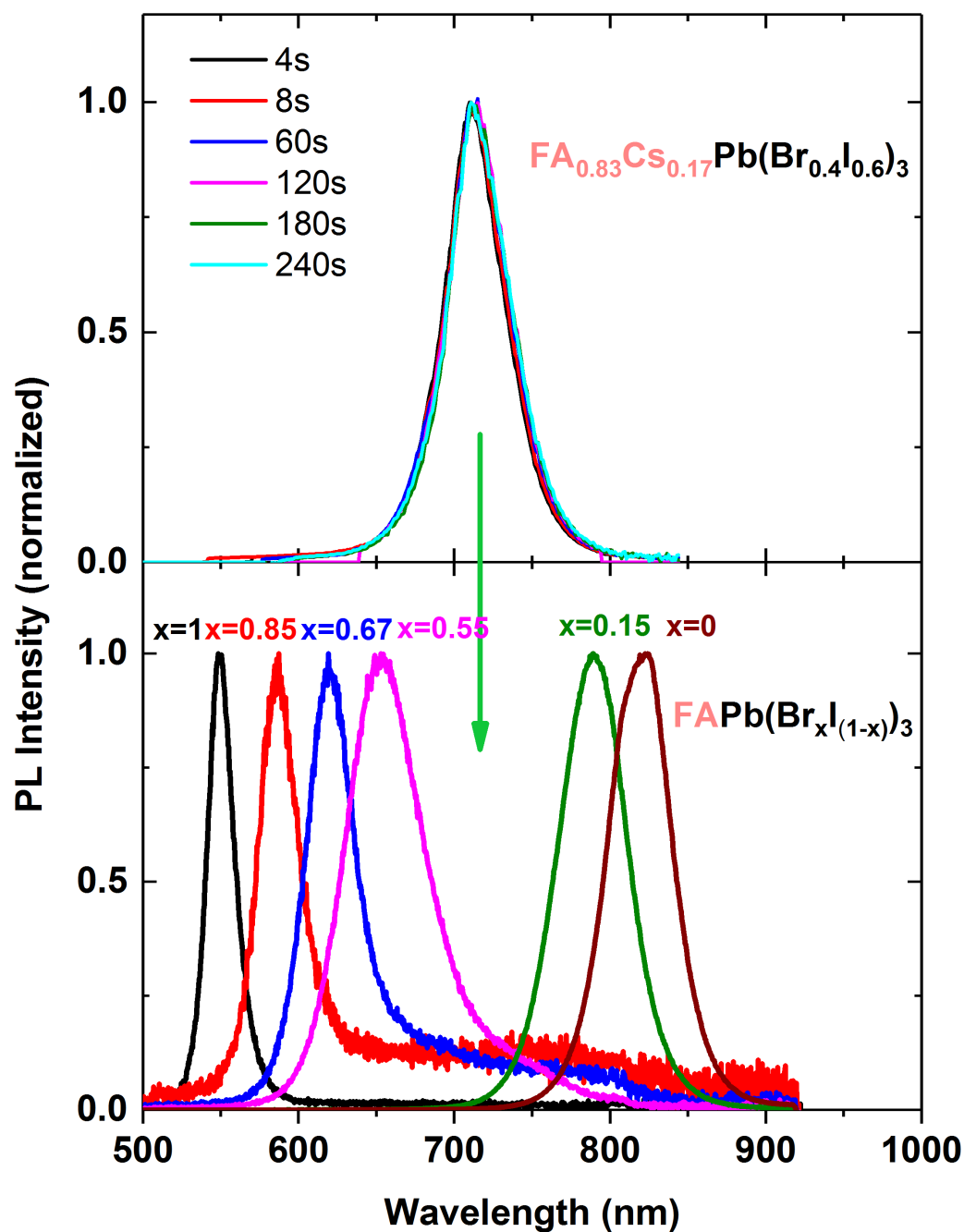


Figure 5.5: The top figure shows the PL spectra of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ following a five-minute excitation with pulse fluence of $0.5 \mu\text{J cm}^{-2}$ and laser intensity of 5 W cm^{-2} at a wavelength of 405 nm. As a comparison, the bottom figure displays previous results obtained for the single-cation $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ series taken from figure 4.1a. The large arrow (green) points towards the intermediate phase gap, which has been partially closed by the mixed-cation film developed in this work.

5.2.2 Electronic Characterisation

As a next step, electronic parameters of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ are investigated. Ultrafast OPTP spectroscopy is performed as a non-contact photoconductivity probe for the ultimate purpose of extracting recombination rate constants and the effective charge-carrier mobility in the material. In Figure 5.6, the fluence-dependent THz photoconductivity transients display an accelerating decay dynamics at higher initial charge-carrier densities, due to stronger contributions from bimolecular and Auger recombination. The rate constants associated with different recombination mechanisms are extracted by global fits to these transient by solving the rate equation described in the previous chapter. Remarkably, compared to single-cation mixed-halide films analysed in the previous chapter (Figure 4.9), the higher order recombination rate constants in this mixed-cation mixed-halide $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ material are suppressed even further, virtually by an order of magnitude. What is more, this film is found to exhibit an excellent charge-carrier mobility of $21 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which drastically outperforms the amorphous and energetically disordered single-cation equivalent $\text{FAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$, which delivers strongly limited charge-carrier mobilities of only $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In the wider scope, the mobility of the mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite investigated here is clearly located in an intermediate range to those ascertained in the previous chapter for FAPbI_3 ($27 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and FAPbBr_3 ($14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which indicates a considerable reduction of structural disorder. The monomolecular recombination rate k_1 is extracted from mono-exponential fits to the tails of the low-fluence PL decay trace measured by TCSPC (Figure 5.7). k_1 largely emanates from trap-assisted charge-carrier recombination which dominates in the lower charge-carrier density regimes. Accordingly, the charge-carrier lifetime of this particular mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite is found to be at a relatively high value of $\tau = 157 \text{ ns}$.

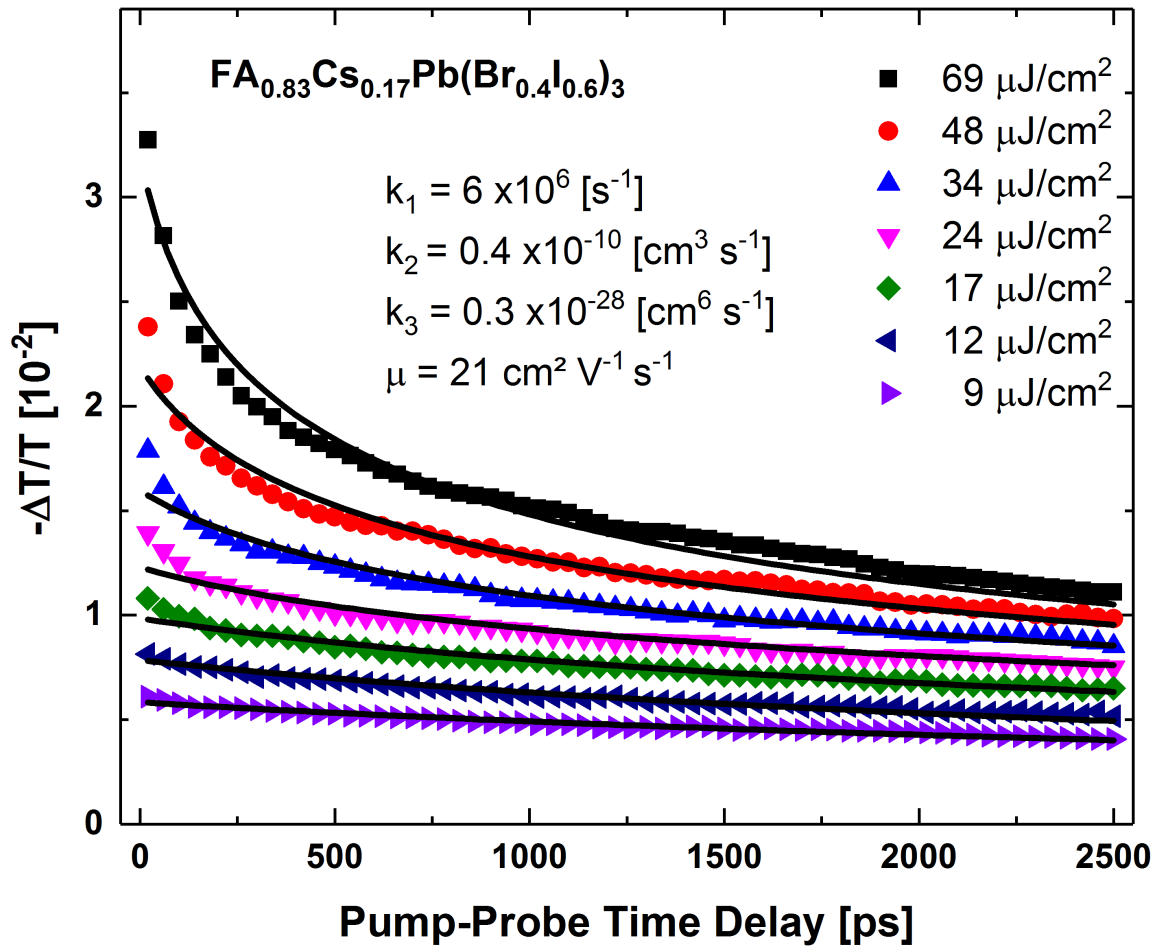


Figure 5.6: Fluence-dependent THz photoconductivity transients for a $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin film, measured at an excitation wavelength of 400nm. The symbols represent data points, and the solid lines are fits as described in the text.

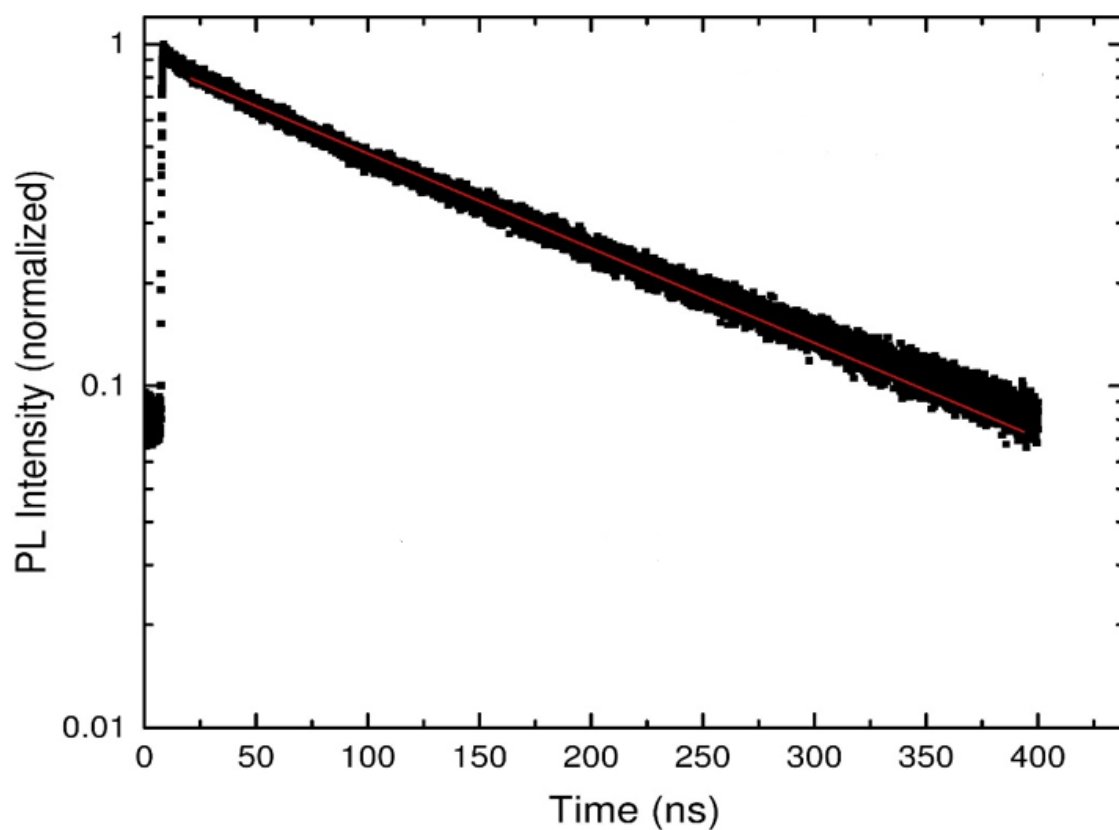


Figure 5.7: Time-resolved PL spectroscopy of a mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin film performed to determine the monomolecular recombination rate constants k_1 extracted from monoexponential fits to the PL decay traces. Excitation fluence was set at $0.077 \mu\text{J cm}^{-2}$ at an excitation wavelength of 400nm.

To also assess the potential of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ for incorporation into a planar heterojunction solar cell architecture, the charge-carrier diffusion length is derived as a function of the charge-carrier density n , where for charge-carrier densities typical under solar illumination ($n \approx 10^{15} \text{ cm}^{-3}$) a value of $L \approx 2.9 \mu\text{m}$ is reached (Figure 5.8), which is comparable to values reported for tri-iodide perovskite thin films [104, 105]. With respect to the results obtained, it can be inferred that the high charge-carrier mobility, low recombination rate constants, and long charge-carrier lifetime favourably impinge on the charge-carrier diffusion length, in this way making a good case for the mixed-cation lead mixed-halide perovskite film to be potentially just as effective as a high-quality solar cell absorber based on tri-iodide perovskites.

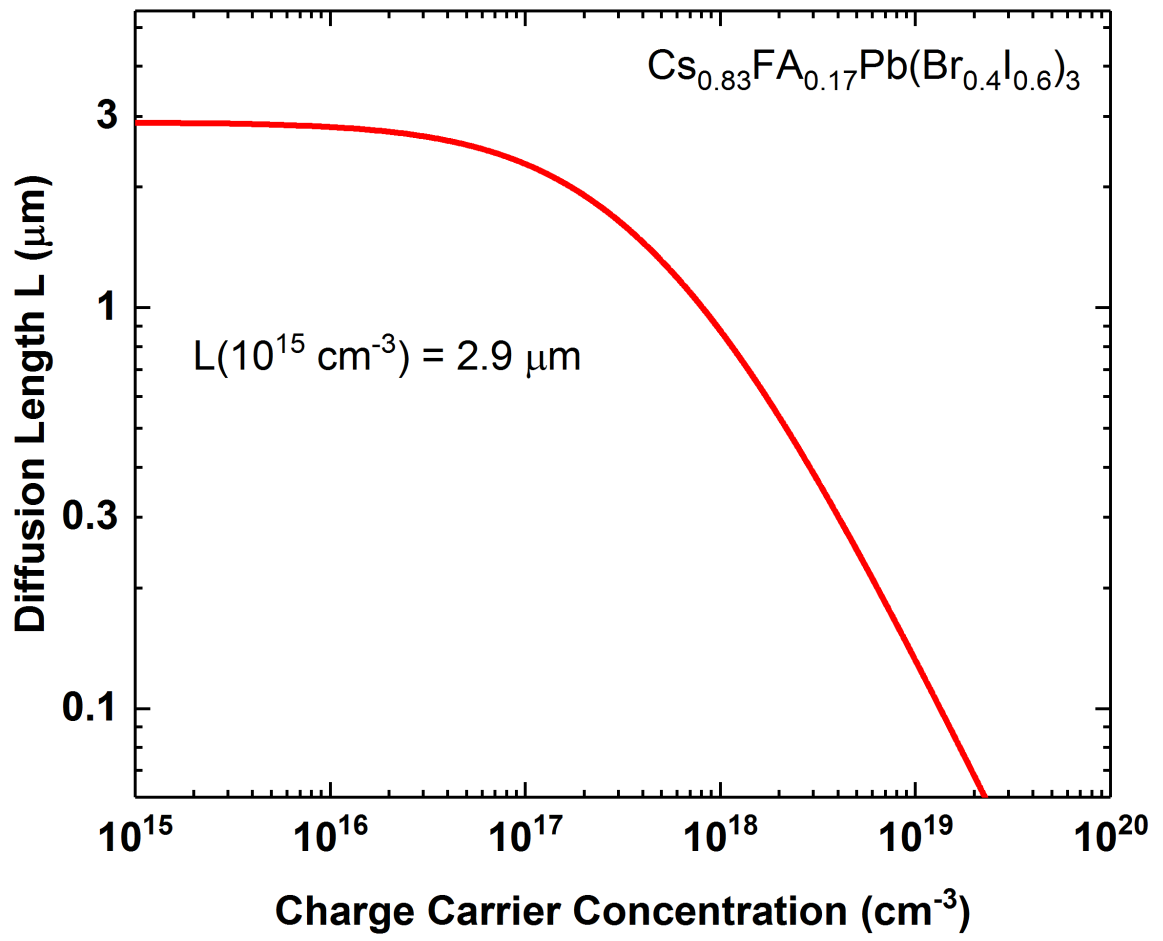


Figure 5.8: Charge-carrier diffusion length L_D of a mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin film as a function of charge-carrier density n .

5.2.3 Photovoltaic Device Performance

A series of planar heterojunction solar cells were fabricated by David P. McMeekin to provide insights into the efficiency output generated by this promising new mixed-cation perovskite material in a photovoltaic device. The device architecture shown in Figure 5.9A consists of a SnO_2 /phenyl- C_{60} -butyric acid methyl ester (PC_{60}BM) electron-selective layer, a solid $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite absorber layer, and Li-TFSI-doped spiro-OMeTAD with 4-tert-butylpyridine (TBP) additive as the hole-collection layer, and an Ag electrode as a capping layer on the top. The current-voltage (I-V) characteristics of the devices were measured under typically solar-relevant conditions, namely simulated AM1.5 and 100 mW cm^{-2} sunlight illumination. The I-V curve of the device with the best obtained results is displayed in Figure 5.9B. With a short-circuit current density of 19.4 mA cm^{-2} and an open-circuit voltage V_{OC} of 1.2 V, this device achieved an extraordinarily high PCE of 17.1%. In order to explore the feasibility of this mixed-cation material as a top-subcell in a tandem solar cell device, a semitransparent $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite solar cell was built by sputter-coating indium tin oxide on top of the perovskite. This device still asserts a PCE of 15.1%. Despite the slight decrease in efficiency compared to the Ag electrode-capped device, the similar short-circuit current J_{SC} suggests that the loss is imposed by the applied sputter deposition technique still requiring further optimisation. Furthermore, the I-V curve of a silicon heterojunction solar cell was acquired, first with and then without the semi-transparent perovskite cell put in front of it. A PCE of 7.3% could be obtained after filtering the light through the semi-transparent perovskite solar cell and 19.2% were achieved in an unfiltered mode of operation. Judging by these results, one can clearly take note of the 7.3% efficiency boost facilitated by using the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ top-subcell on the silicon heterojunction device.

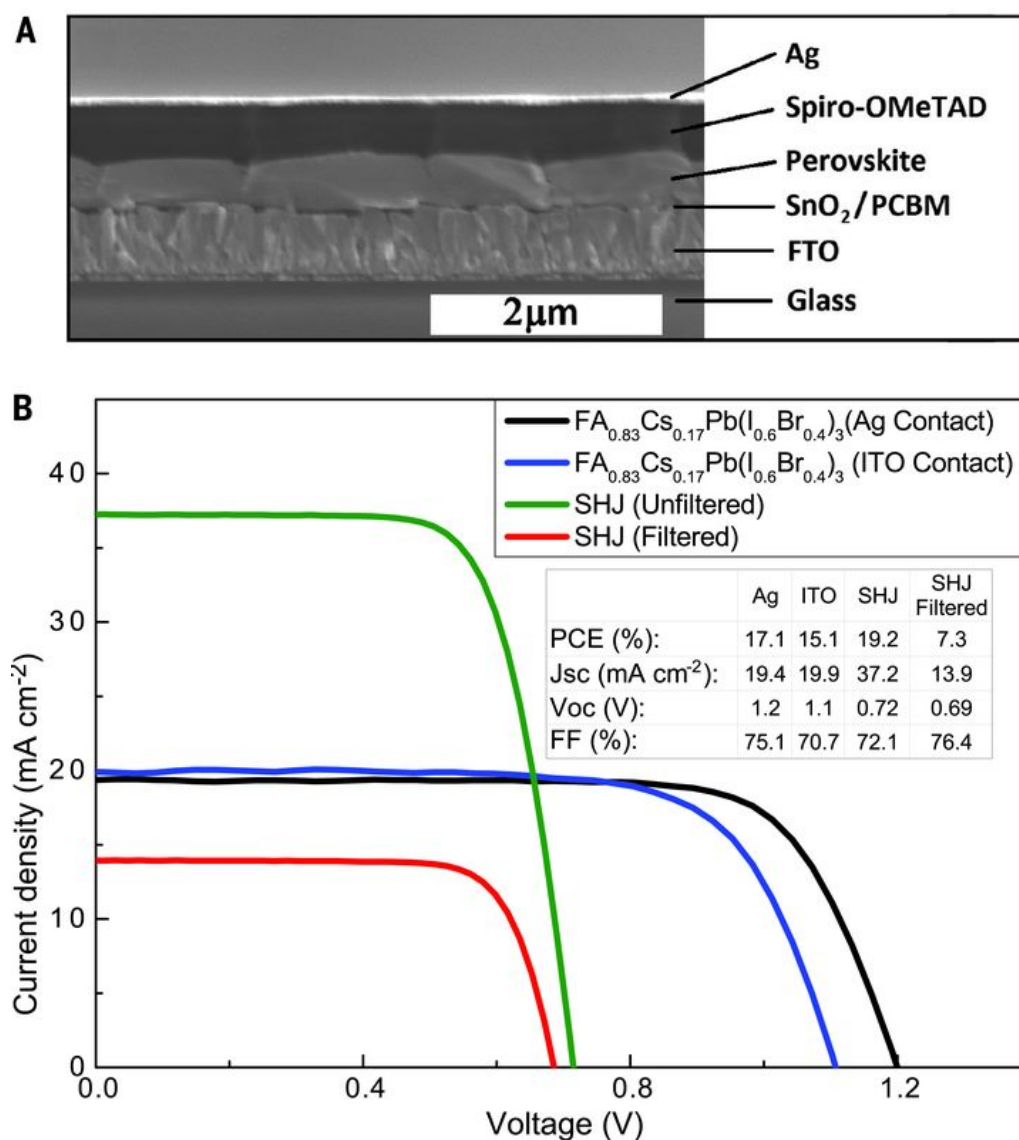


Figure 5.9: (A) Scanning electron microscope cross-section of a mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin film planar heterojunction solar cell device. (B) I-V curve for the highest-performing perovskite devices fabricated, using either a Ag metal or semi-transparent ITO top electrode, measured at a scan rate of 0.38 V s^{-1} (Forward bias to short-circuit). The I-V curve of SHJ cells were measured with direct light or with simulated sunlight filtered through the semi-transparent perovskite solar cell. SHJ cells measurements were undertaken at the Centre For Renewable Energy Technologies, Loughborough, UK, under a well-calibrated solar simulator. All other pertinent data acquisition and device fabrication were performed by David P. McMeekin.

5.2.4 Crystallization Kinetics and Charge-Carrier Transport

With the objective of making better quality films, this section investigates how adding hydrohalic acids to mixed-cation lead mixed-halide $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$ perovskite precursor solution influences the formation of thin films. Several reports indicate the benefits of using hydrohalic acids for creating smoother films, improving their surface coverage [18, 184] or enhancing crystal structure [185]. Although, there is only rudimentary understanding of what effectuates this encouraging behaviour, it is assumed that the usage of such additives tunes the colloids concentration present in the precursor solution which in turn govern nucleation sites and crystallization kinetics of the perovskite. An increasing number of reports suggest a stark correlation between crystallinity/grain sizes and the performance of perovskite absorber layers [86, 186]. Given the multitude of potentially beneficial effects of using acidic additives, it is logical to assume that these patterns are also conferrable to the optoelectronic nature of perovskite materials, which is matter of investigation in this sub-chapter. Considering the interlinked nature of all involved factors, it comes down to systematically unraveling the underlying correlations for gaining insights into ways to ultimately improve film fabrication.

The research subject for ensuing investigations is a mixed-cation lead mixed-halide $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$ perovskite. Its precursor solution consisting of CsI, FAI, PbBr_2 , and PbI_2 is prepared in DMF with the aim to ensure a molar ratio of 0.83:0.17:0.2:0.8 for FA:Cs:Br:I at a 1.15 molar concentration. Moreover, HI and HBr acids are added to the solution aiding to attain a halogen molar ratio of 8:2, causing a volume concentration of $81.7 \mu\text{L mL}^{-1}$ of HI (57 wt% in H_2O) and $17.6 \mu\text{L mL}^{-1}$ of HBr (48 wt% in H_2O). After preparation and initial addition of acid, the precursor solution was stored in a nitrogen atmosphere and their intensity distribu-

tion was monitored for a stipulated time period. The solutions were all prepared by David P. McMeekin.

In a matter of days, a vanishing of the initially present large micrometer-size particle distribution (colloids) upon adding hydrohalic acids is measured by Dynamic Light Scattering (Figure 5.10) with a Malvern Zetasizer Nano ZS. The measurement was conducted with a quartz cuvette at room temperature conditions.

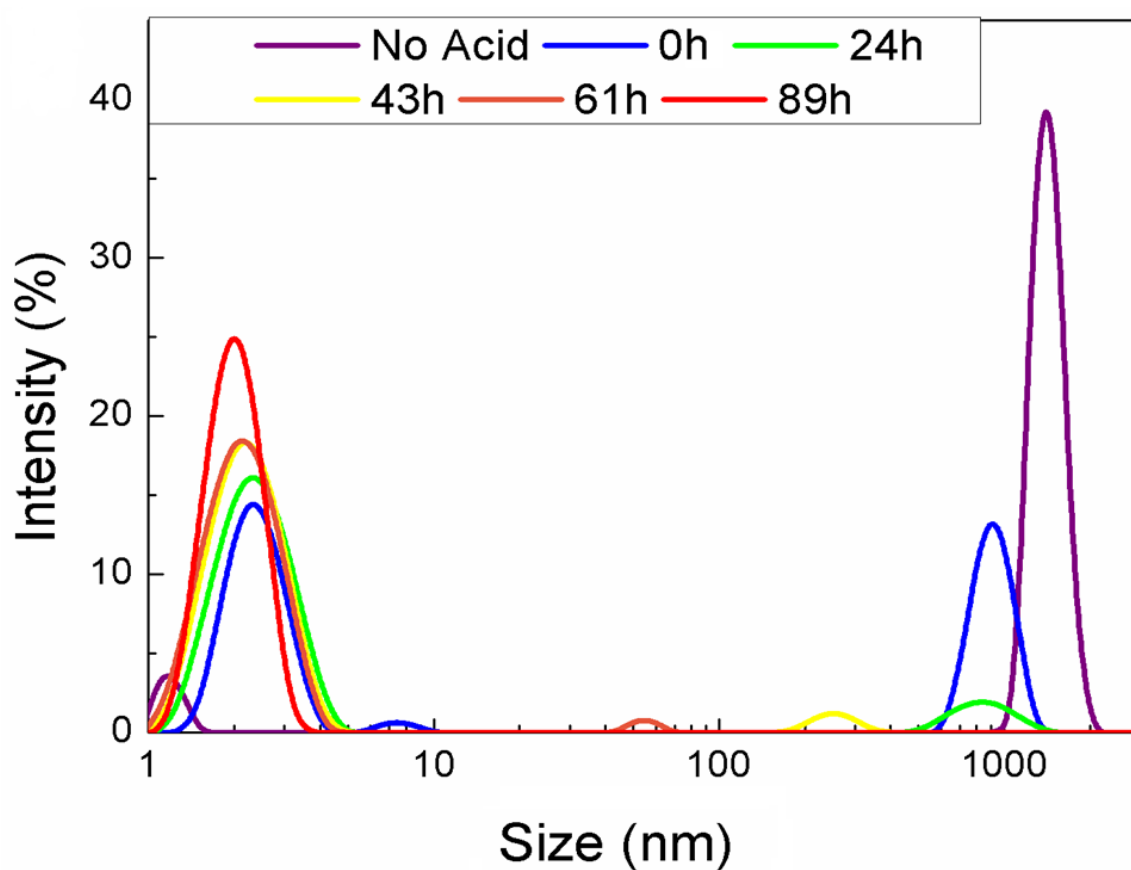


Figure 5.10: Size distribution of colloidal hydrodynamic particles in FA_{0.83}Cs_{0.17}Pb(Br_{0.2}I_{0.8})₃ perovskite precursor solutions as a function of aging time. The measurement was done via dynamic light scattering. The data was taken by David P. McMeekin.

The fundamental impact of the colloids concentration on the morphology and grain size/crystallinity of the perovskite film is illustrated in Figure 5.11A-E, where scanning electron microscopy images of the perovskite films after different aging times are compared to each other. The films are deposited on fluorinated tin oxide substrates. The precursor solution of the film shown in Figure 5.11A was free of acidic additives and thus forms a film with large amounts of pinholes and intergranular cracking. The addition of acids triggers a process which enables the lead polyhalide colloidal framework to dissolve gradually, allowing for a change in crystal growth, nucleation dynamics and thus film morphology. Keeping track of this over a given time period (for a few days), a significant enlarging of crystal grain sizes from roughly 100 nm prior to the addition of acids up to a few micrometers for colloid-free solutions under identical annealing conditions could be observed. However, the last figure of this series (Figure 5.11E) reveals how cube-like crystal grains are formed with distinguishable boundaries when annealed at higher temperatures, indicating a reversal point, which basically marks the starting point of a possibly negative trade-off between grain size and morphology (pin-hole density) at this point of colloids distribution.

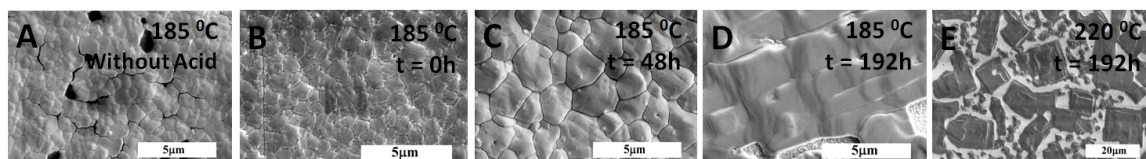


Figure 5.11: Impact of colloids in the precursor solution on crystal grain sizes and material morphology in $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$ films. A-E) A series of top-view scanning electron microscope images of a fully annealed $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$ perovskite thin film prepared with or without hydrohalic acids subjected to a rigid, time-dependent aging protocol.

In a following step, thin film samples from different precursor solutions with varying colloidal concentrations were prepared. The absorption spectra thereof are displayed in Figure 5.12. Except for the 0h aged sample (red), all other films display sharp absorption onsets. In Figure 5.13 the effective charge-carrier mobility of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$ films measured from optical pump - THz probe spectroscopy are presented. The measured charge-carrier mobilities increase by more than 100% (from <10 to $>20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) when comparing films processed from precursor solutions with lower levels of colloids concentration to higher amounts of colloids. The effective carrier mobilities have been corrected by scaling the onset value of $\frac{\Delta T}{T}$ with the relative surface coverage of the respective films, which were obtained by processing the SEM images presented in Figure 5.11. The surface coverage remains high ($> 98\%$) for most of the aged films, but drops off to $\approx 80\%$ for the 168h aged films. Although, the two 168h aged films form the largest crystal grain sizes, they also tend to build up more pinholes. Although, this is accounted for by performing the surface correction, the plateauing trend can still not be reversed, suggesting that at this point the negative trade-off between crystal grain sizes and film morphology becomes more severe. Due to high absorption coefficients in these materials most of the light is being absorbed within the first hundreds of nanometers, for which reason an additional thickness correction is not required, especially since the thickness of all measured films exceeds 400 nm.

The charge-carrier mobility values obtained in this study, excellently showcase the impact of colloids concentration in the precursor solution on the electronic properties of the perovskite material. The demonstrated increase in charge-carrier mobilities also stands in good agreement with observations made for increasing crystalline quality/grain sizes and film morphology upon applying the aging protocol (Figure 5.11A-E).

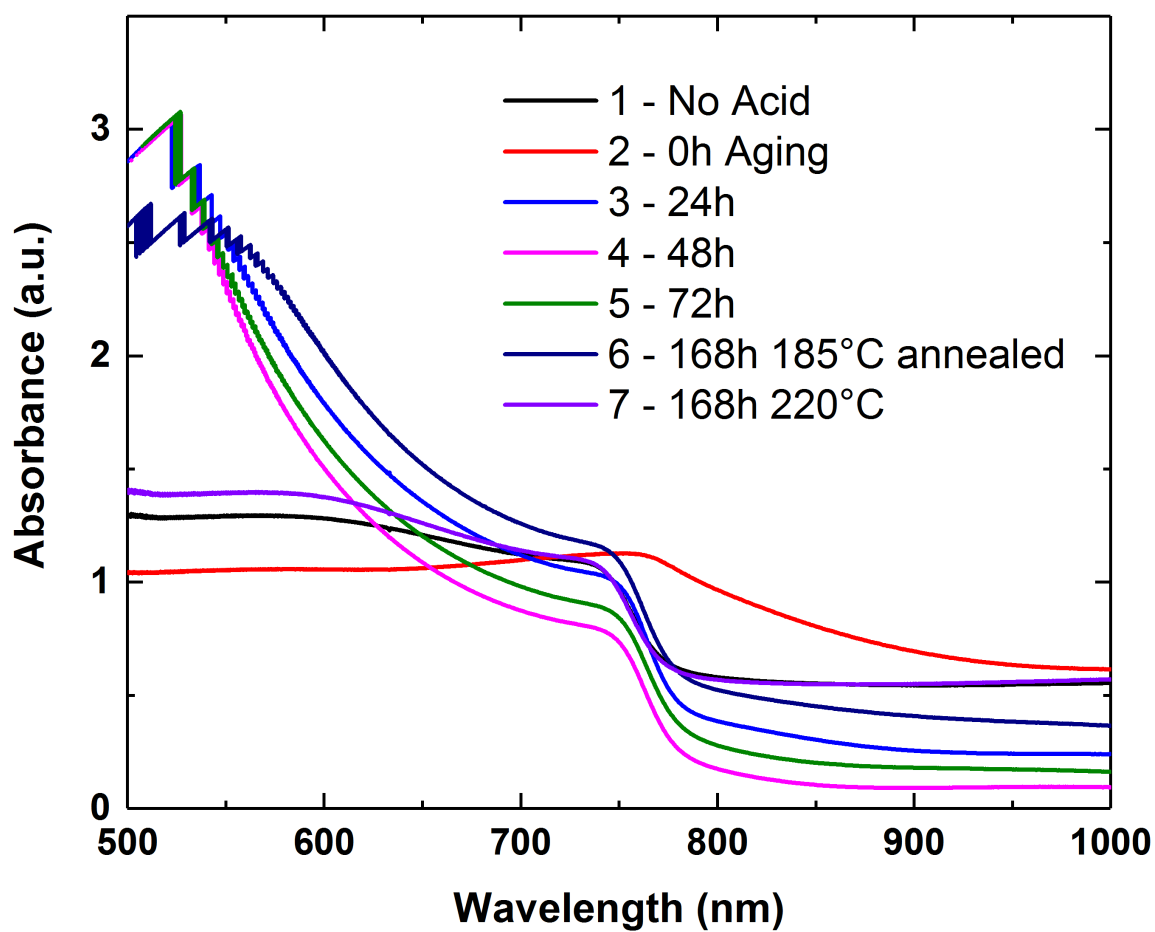


Figure 5.12: Absorbance spectra of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ films made of precursor solutions with varying colloids concentrations. The data were obtained by measuring the optical transmission and reflection using a Fourier-transform infrared spectrometer.

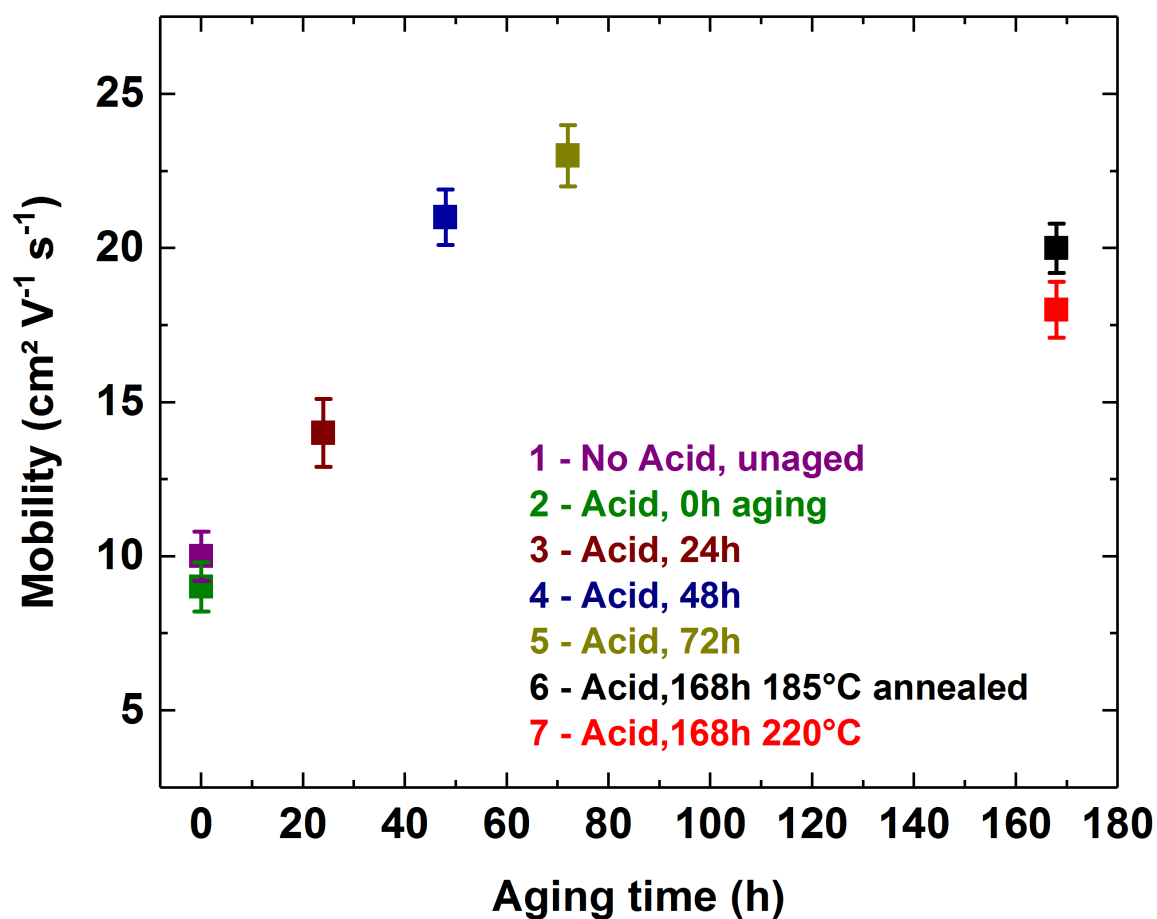


Figure 5.13: Impact of colloids concentration on electronic properties in $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$ films. Surface coverage-corrected effective charge-carrier mobilities derived from THz spectroscopy measurements for perovskite films fabricated from precursor solutions with different colloids concentration. Error bars indicate the range of values obtained.

5.2.5 Conclusions

This work highlights the strongly competitive nature of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ mixed-cation lead mixed-halide perovskites, with A-site cation-mixing introducing a new method for readily achieving potentially stable and highly-efficient films comparable to the best reported single-junction perovskite solar cells reported so far [187, 188]. Astonishingly, despite the wider band gap of 1.74 eV in this material, the efficiency loss with respect to the ideal bandgap for single-junction solar cell devices [189] could be constrained, thanks to the high level of structural stabilisation and favourable optoelectronic properties achieved, which altogether contribute to sparking off PCEs in the range of 17%.

Especially, in a tandem solar cell configuration, this 1.74 eV mixed-cation mixed-halide $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ composition is capable of generating a higher V_{OC} than the 1.55 eV MAPbI_3 tri-iodide perovskite employed in a planar heterojunction solar cell design. In view of calculations made by Rau et al. [190], integrating the external quantum efficiency over the entire blackbody radiation spectrum, yields a maximum achievable V_{OC} of 1.42 V for the device reported in this work, which is roughly 100 mV higher than the estimate made by Tvingstedt et al. and Tress et al. for MAPbI_3 solar cell devices [187, 188]. Further improvements in terms of perovskite film quality, device integration, and carefully choosing the most suitable silicon bottom-subcell, would certainly help to improve chances of making a tandem-design system that is more than 30% efficient.

Besides, the impact of colloids concentration in the precursor solution of a mixed-cation lead mixed-halide $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite on the nucleation and growth kinetics of the crystal structure was explored. A systematically applied time-dependent solution aging protocol turns out to be an adequate method for quantifying and controlling the size and dispersion of colloids in the precursor solution, which could effectively be put in relation with a remarkable increase in crystallinity, film morphology and a twofold rise of charge-carrier mobility.

Chapter 6

Mixed-Cation Lead Mixed-Halide Perovskites: Links between Crystallinity, Photo-Stability and Electronic Properties

Mixed-halide bromide-iodide perovskites are an important material class that can allow a 1.75 eV bandgap crucial for integration with silicon in tandem cells [59]. However, both MA and FA versions of lead mixed-halide perovskites have been found to be unstable under illumination, with the material segregating into iodide-rich and bromide-rich regions [93]. In the preceding chapter, a mixed-cation lead mixed-halide $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite with 1.74 eV bandgap that allowed for $\approx 17\%$ PCE in a single-junction device and exhibited low disorder, long charge-carrier lifetimes and high mobilities could be demonstrated successfully. These mixed-cation mixed-halide perovskites could be crystallised at much higher temperatures than previously reported hybrid perovskites, which lead to materials with high levels of crystallinity, as judged by XRD measurements. Importantly, this material appeared not to suffer from halide-segregation, which had previously marred prospects for wide-band gap mixed halide perovskites. This finding, along with observations by Zhou et al., suggests that enhanced crystallinity may open a pathway towards suppressing halide segregation and creating a perovskite absorber material which can sustain a

wide band gap and high open-circuit voltage [191].

In this chapter, such links are explored by looking at a wide parameter space in the mixed-cation, mixed-halide $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ perovskite. The prominent causes behind boundaries and transitions between different alloying regions with structural instability are thoroughly examined. Furthermore, a strong link between crystallinity and optoelectronic properties such as trap-related recombination and charge-carrier mobility is highlighted. Crucially, it is established that materials in regions of enhanced crystallinity are also more stable against photo-induced halide segregation. The findings also demonstrate that crystal interfaces in the perovskite play a determining role in nucleating such halide segregation. Careful control over grain boundaries may therefore be sufficient to eliminate such effects, giving rise to photo-stable materials.

6.1 Sample Preparation

6.1.1 Perovskite Precursor Solution Mixture

The solutions were prepared by using FAI, FABr, CsI and CsBr, PbBr_2 and PbI_2 which were dissolved in DMF to achieve the stoichiometric solution desired for making $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ compositions. All solutions were aged for approximately 48h after addition of HI, HBr or a mixture of both. Acid concentrations were adjusted according to the molarity of the solution and the halide composition of the precursor salts. To obtain a series of $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ precursor solutions, two stoichiometric precursor solutions with fixed 40/60 Br-I halide ratios were mixed, but with various FA/Cs cation ratios. To obtain a series of $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ pre-

cursor solutions, two stoichiometric precursor solutions with fixed 83/17 FA/Cs cation ratios were mixed, but with various Br-I halide ratios. All solutions were prepared by David P. McMeekin.

6.1.2 Film Fabrication

The precursor perovskite solution was spin-coated in a nitrogen-filled glovebox at 2000 rpm for 45s, on a substrate pre-heated at 70°C. Immediately after spincoating, the films were dried inside a N₂ glovebox on a hot plate at a temperature of 70°C for 1 minute. All films, with the exception of CsPb(Br_{0.4}I_{0.6})₃, were then annealed in an oven in an air atmosphere at 185°C for 90 minutes. CsPb(Br_{0.4}I_{0.6})₃ films were annealed inside N₂ at 185°C for 30m. All samples were prepared by David P. McMeekin.

6.2 Results and Discussion

6.2.1 Optoelectronics and Stability of Cs_yFA_(1-y)Pb(Br_{0.4}I_{0.6})₃

The study is commenced by first characterizing the structural stability of the mixed-cation series Cs_yFA_(1-y)Pb(Br_{0.4}I_{0.6})₃ with Cs content y varying between 0 and 0.8. Figure 6.1 shows sample XRD patterns for four Cs_yFA_(1-y)Pb(Br_{0.4}I_{0.6})₃ films with different Cs fractions $y = 0.01, 0.05, 0.20, 0.60$; more spectra covering the full range of y are shown in Figure 6.2. The (100) and (200) reflections off the Cs_yFA_(1-y)Pb(Br_{0.4}I_{0.6})₃ perovskite are clearly visible near $2\theta \approx 14^\circ - 15^\circ$ and $28^\circ - 30^\circ$. However, additional diffraction peaks can also be observed, in particular for low and high caesium content. These peaks are identified as belonging to the yellow hexagonal δ -phase (δ_H), which

features for the FA-rich samples, and to the orthorhombic δ -phase (δ_O) which contributes at the Cs-rich end of the series. For ease of identification, Figure 6.3 presents XRD patterns of tri-iodide and mixed-halide FAPbX_3 and CsPbX_3 films that have most definitely converted into the yellow δ -phase.

Increasing the Cs content from 0 to 5% (Figure 6.1b) leads to a marked reduction in such inclusions while at 20% Cs content (Figure 6.1c) they are mostly, but not entirely, suppressed, and the XRD spectrum exhibits strong, sharp perovskite α -phase peaks. By examining in suitably small steps of the full Cs concentration range, it is found that the (100) reflection has the highest intensity for $\text{Cs}_{0.2}\text{FA}_{0.8}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ ($y = 0.2$), indicating the highly crystalline nature at this particular caesium fraction (Figure 6.4). The peak intensity in counts increases by an order of magnitude even compared to neighbouring Cs concentrations on the left and right. Beyond $y = 0.2$, the perovskite diffraction amplitude declines, and reflections assigned to the yellow δ_O -phase, associated with Cs-rich films, appear. At $y = 0.60$, the crystal structure is still relatively strongly oriented and ordered, however, the δ_O phase emerges and adversely affects the crystallinity of the material (Figure 6.1d).

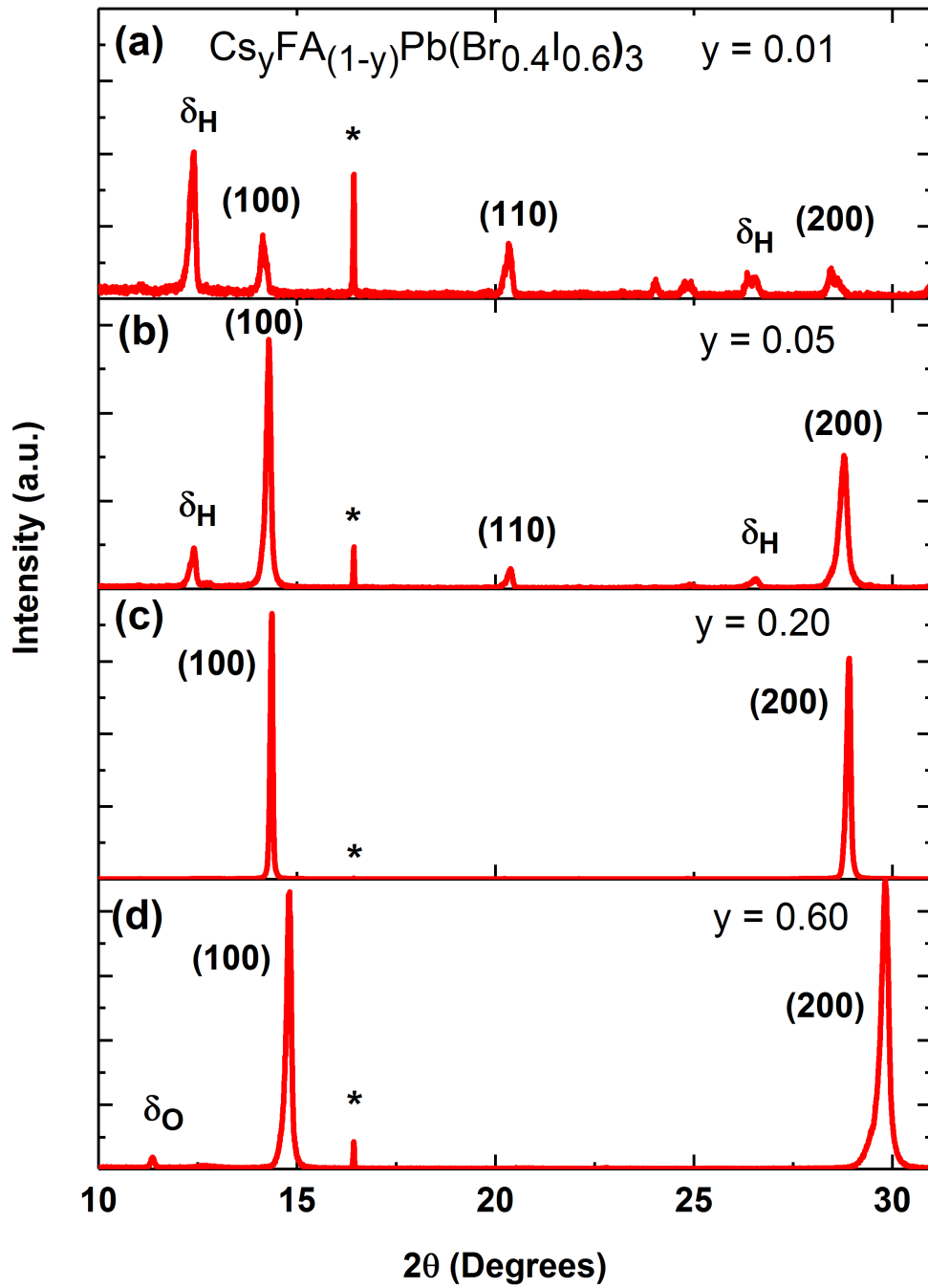


Figure 6.1: X-ray diffraction (XRD) patterns of four different $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite films with Cs content varying as (a) $y = 0.01$, (b) $y = 0.05$, (c) $y = 0.20$ and (d) $y = 0.60$. δ_H and δ_O denote diffraction peaks from the hexagonal δ -phase of FA-rich $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ and the orthorhombic δ -phase of Cs-rich $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$, while (*) marks diffraction patterns related to the z-cut quartz substrates.

This structural instability can be understood in terms of the Goldschmidt tolerance factor for such compounds. While the FAPbI_3 perovskite α -phase exists at the upper end of the tolerance range due to the large ionic radius of FA, the CsPbI_3 perovskite α -phase forms at the lower end; hence both compounds have a tendency to deteriorate into competing δ -phases [81]. Mixing Cs and FA yields structurally stable compounds because the effective ionic A cation radius lies closer to that of MA and therefore is more amenable to the perovskite structure promoting higher crystallinity. Yi et al. theoretically calculated that the mixed Cs/FA cation perovskites should be structurally stable over the entire phase composition [78]. However, the obtained experimental results here suggest that good structural stability is only achieved within the range of $y = 0.1$ to 0.3 .

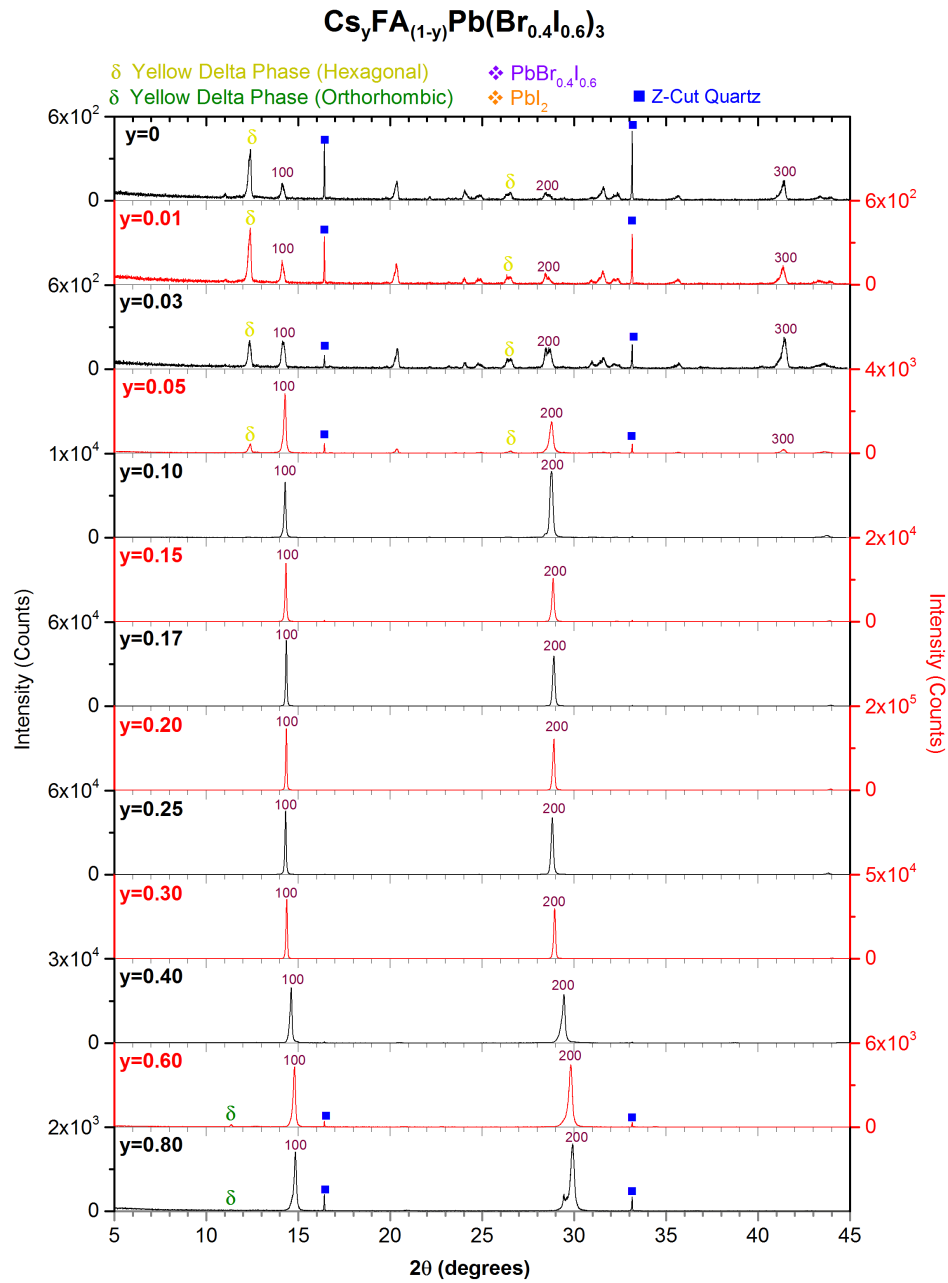


Figure 6.2: X-ray Diffraction patterns of $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin films with varying cesium content ($0 < y < 0.8$). As the concentration of Cs reaches 20%, the intensity of the cubic (100) reflections not only stabilises at $2\theta 14.3^\circ$ but also increases and sharpens.

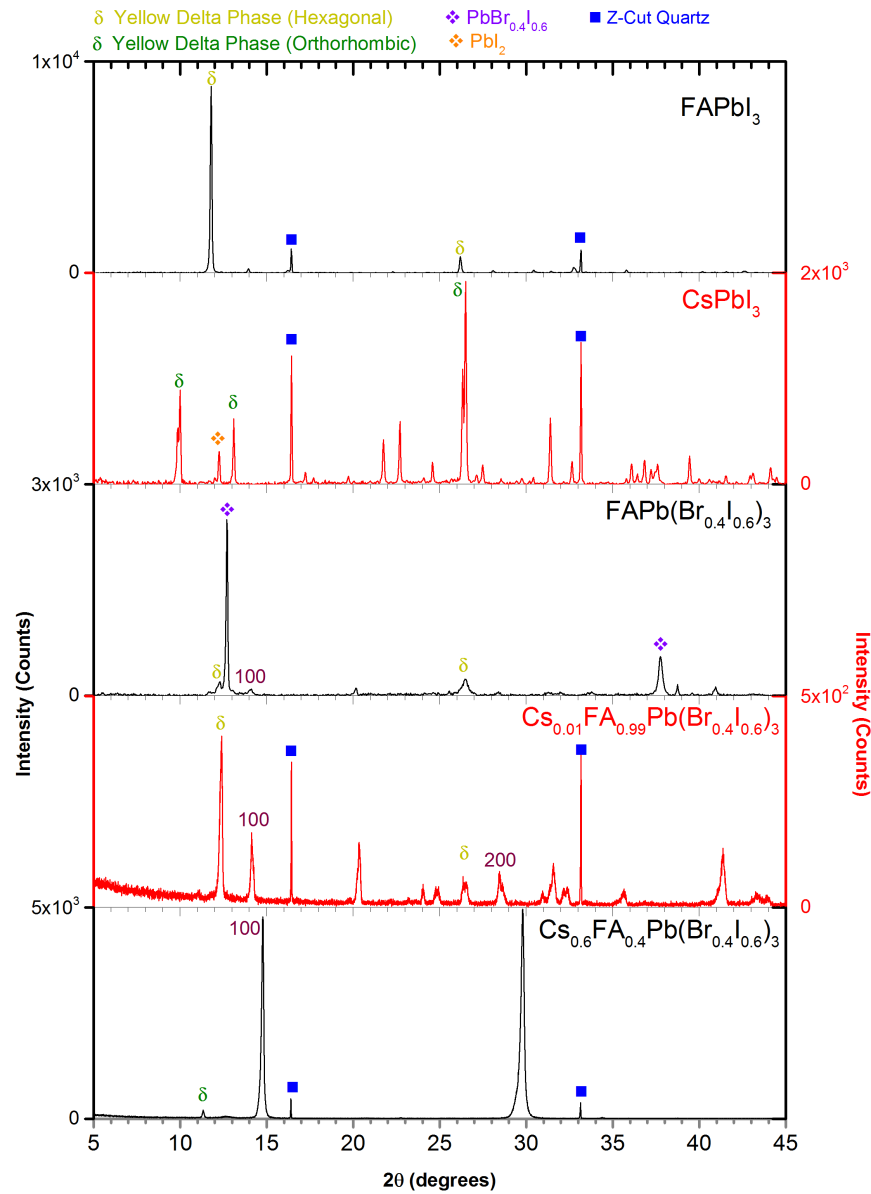


Figure 6.3: X-ray Diffraction patterns of δ -phase FAPbI_3 , δ -phase CsPbI_3 , yellow $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ and the 1% and 60% Cs films used in the study. From the diffraction patterns obtained for the $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$, there are clear reflections from some excess PbI_2 ($2\theta = 12.7^\circ$) and the hexagonal yellow phase of the mixed halide $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ ($2\theta = 12.4^\circ$). The substitution of iodine with bromine results in a contraction of the lattice volume, which explains the shift to a larger 2θ angle from the original hexagonal yellow FAPbI_3 reflection ($2\theta = 11.8^\circ$). This enables us to assign the reflection observed at $2\theta = 12.4^\circ$ with the yellow hexagonal $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$, which are observed in films with very small quantities of Cs (0% - 5%).

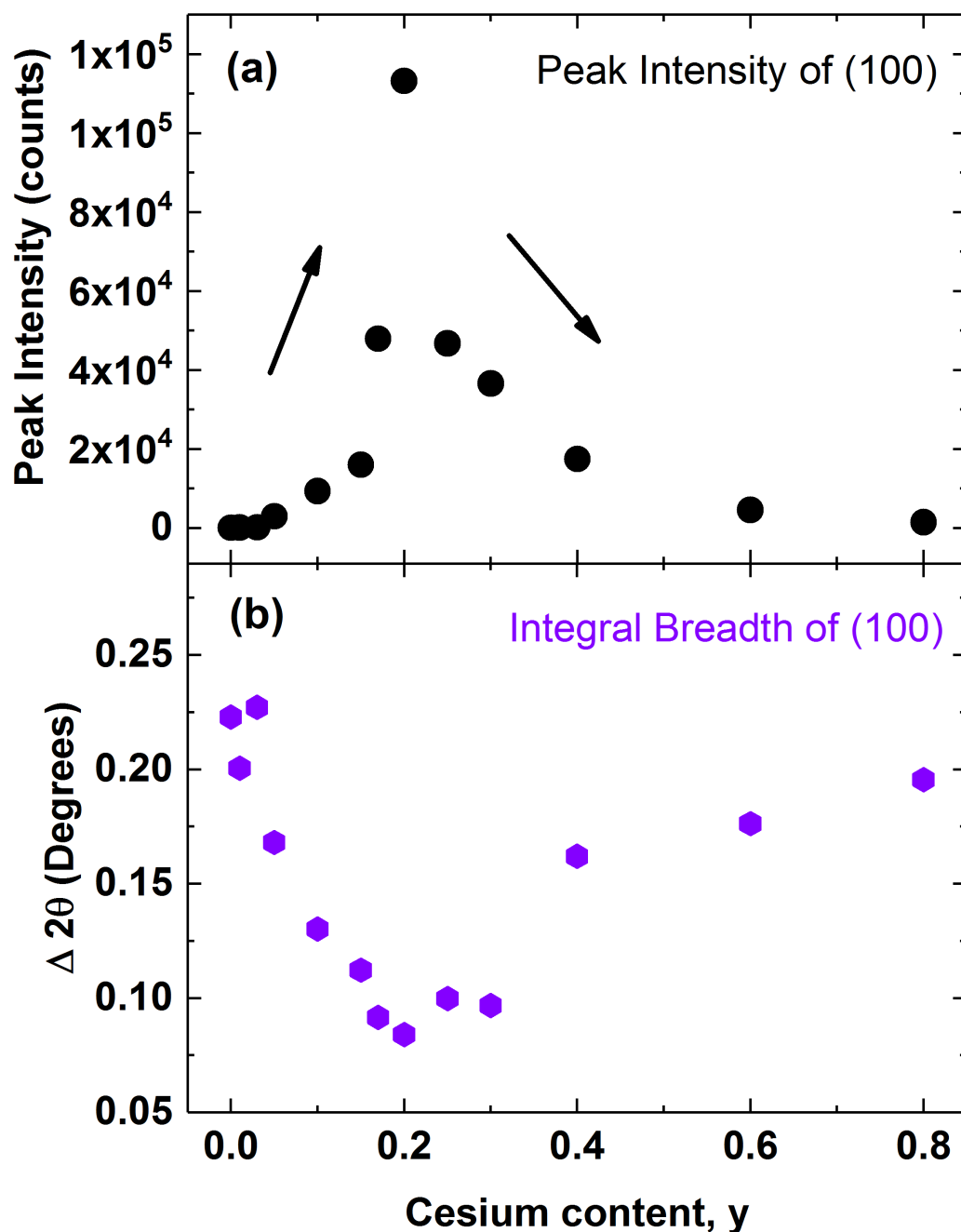


Figure 6.4: (a) Intensity change of the (100) reflection peak as a function of the caesium content in $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin films. This is a clear indication of the films encompassing strong crystalline domains between Cs 17% - 25%. Thereafter, further addition of Cs shows large shifts of the cubic reflection and a reduction in Intensity and broadening of the peak. (b) Integral Breadth of the (100) reflection peak as a function of the Cs content in $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin films.

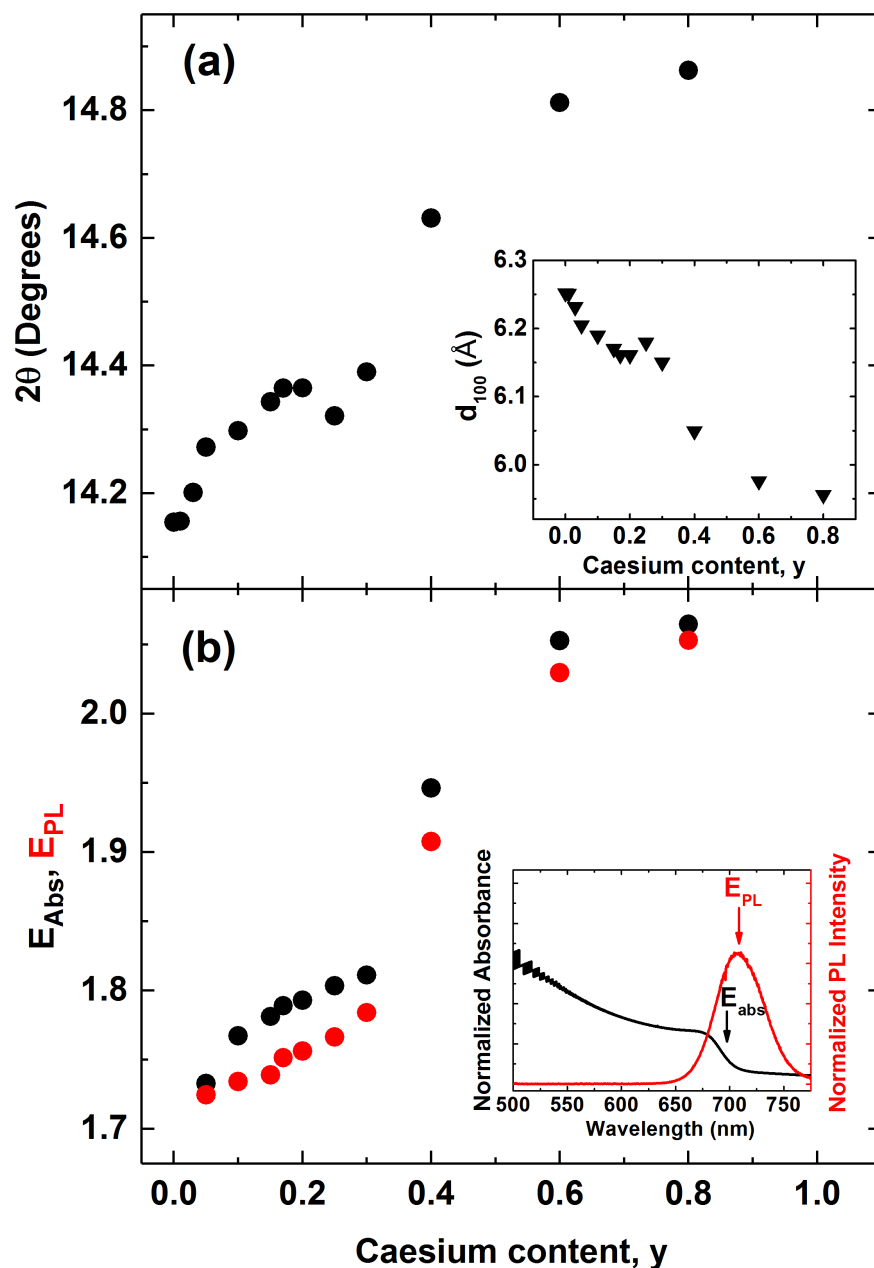


Figure 6.5: (a) Shift of the cubic (100) reflection peak in $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite with varying Cs content ($0 < y < 0.8$) taken from XRD spectra in Figure 1. Inset: Value of the (100) crystallographic plane separation with varying Cs content derived from the scattering angle (Bragg's law) (b) absorbance onset values E_{Abs} (black dots), determined from the maximum of the differential of the absorbance spectra near the absorption edge taken with Fourier transform infrared spectroscopy (shown in Figure 6.7). PL peak positions E_{PL} (red dots) were taken from in situ steady-state PL spectra (shown in Figure 6.6) following excitation at 400 nm with an intensity of 14.9 mW cm^{-2} (fluence of $13.5 \text{ } \mu\text{J cm}^{-2}$, pulse duration 40 fs, repetition rate 1.1 kHz).

An additional factor influencing mixed Cs/FA perovskites is the internal distortions that may arise when ions of such differing ionic radii are distributed across the A cation sites. Clear indications for such distortion are discovered here, as for example in the slight splitting of the perovskite reflection peak visible at 29.8° for 80% Cs inclusion (Figure 6.2). In addition, it is found that the pseudo-cubic lattice parameter derived from the peak shift of the (100) XRD reflection changes in a non-linear manner with caesium content. Figure 6.5a displays the observed (100) peak shift from 14.2° to 14.9° , and the associated (Bragg's law) lattice parameter reduction from 6.25 to 5.96 Å over the entire compositional range under study. The reduction of the pseudo-cubic cell volume with increasing incorporation of the smaller Cs cation results from a stronger interaction between the A cation and X halides [79]. In addition, it may increase the cationic charge of PbI_2 ions, thus changing the bonding nature between PbI_2 and halides in the 3D perovskite [192]. Interestingly, the (100) diffraction peak shifts with Cs content in a distinctly nonlinear manner. The associated lattice parameter (Figure 6.5a, inset) first decreases relatively gently towards 30%, but then drops abruptly beyond. This behaviour is markedly different from MA-to-FA organic cation and Br-to-I halide substitutions [18, 193] for which linear shifts in lattice parameter (Vegard's law) are generally observed. The non-linear shift observed here can be attributed to the substantial mismatch between the ionic radii of Cs and FA (0.98 Å), which is an order of magnitude larger than that between MA and FA (0.09 Å) and approximately five times larger than the difference between Br and I (0.21 Å) [42, 194].

As a result, the lattice may become extremely distorted in particular for the central regions of relatively even Cs and FA contributions, leading to rapid changes in lattice parameter and potentially a change in space group. This observation is corroborated by PL and absorption measurements (Figure 6.5b), which display a similar trend, namely abruptly shifting PL peaks (red dots) and absorption onsets (black dots) between 30 - 60% Cs content. Across the full compositional range, the PL peak energy E_{PL} tunes broadly from 1.72 eV to 2.05 eV. The absorption onsets E_{Abs} are only slightly blue-shifted (by 10 - 40 meV) which suggests that the PL mainly arises from band-edge emission rather than from trap states, or impurity regions rich in iodide (Figure 6.7). Overall, the undertaken investigations demonstrate that the structurally most stable compositions in the $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ series are found in the region for Cs content of $0.1 < y < 0.3$, since within this range only little evidence for Cs or FA yellow phase inclusions is observed.

The influence of Cs/FA composition on the crystallinity of the $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite is illustrated in Figure 6.8a, where the FWHM of the (100) cubic perovskite peaks as a function of Cs content is displayed. According to the Scherrer equation, the broadening of peak widths from XRD patterns are inversely proportional to the mean crystallite size in the films and/or the microstrain [195, 196, 197]. It is found that on adding Cs to $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$, the FWHM decreases by 62% until a global minimum is reached at $y = 0.2$. At the same time, a significant increase in the scattering peak intensity is also observed with the addition of caesium, up to $x = 0.2$, with a subsequent, consistent reduction in scattering intensity with further increases in caesium content (Figure 6.4). Both of these observations, i.e. the narrower peak widths and significant increase in scattering intensity, show that the addition of a small fraction of caesium results in an increased fraction of crystalline material and/or larger crystalline domains. The narrower peak widths may also indicate re-

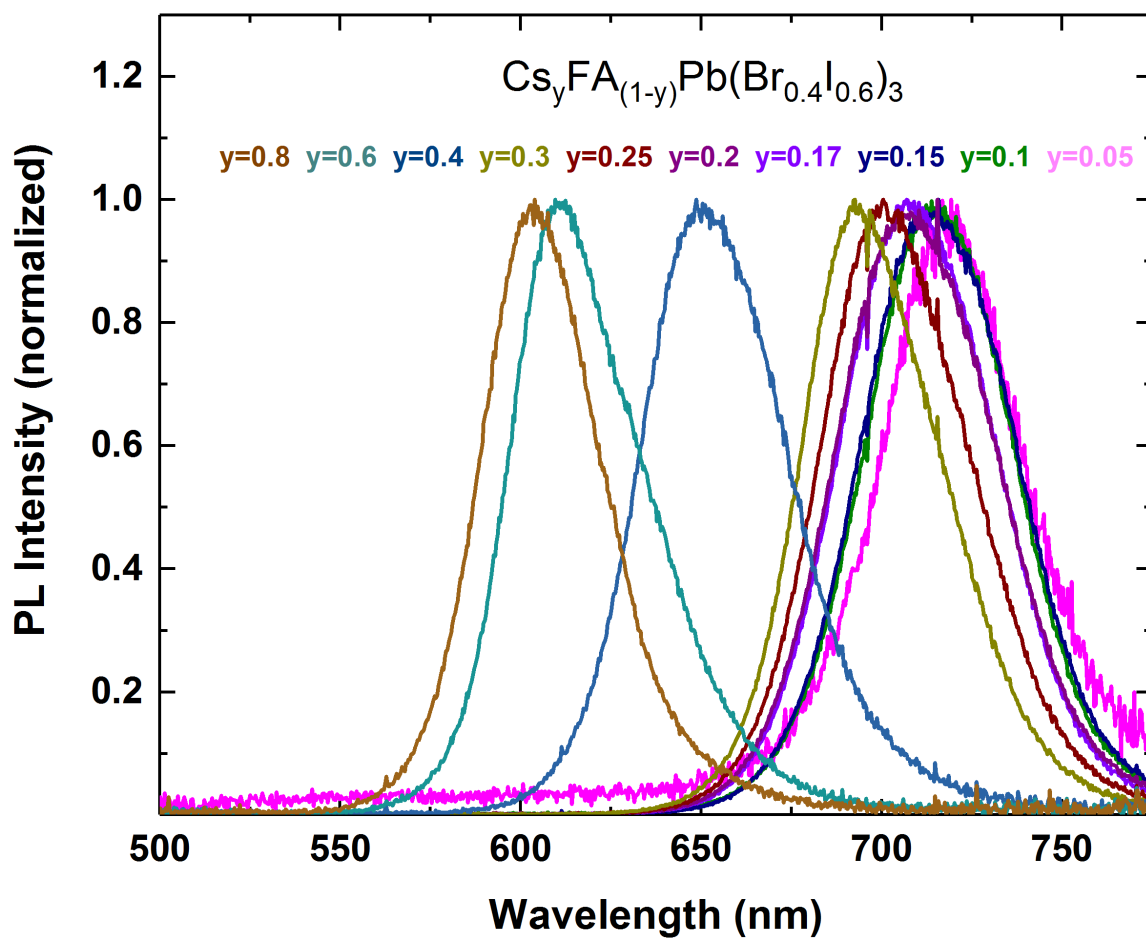


Figure 6.6: Steady-state photoluminescence (PL) spectra of $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ thin films with varying caesium content y , recorded immediately following excitation at 400 nm at a fluence of $13.5 \mu\text{J cm}^{-2}$ (14.9 mW cm^{-2}) under vacuum. The PL spectra have been normalised to the peak emission.

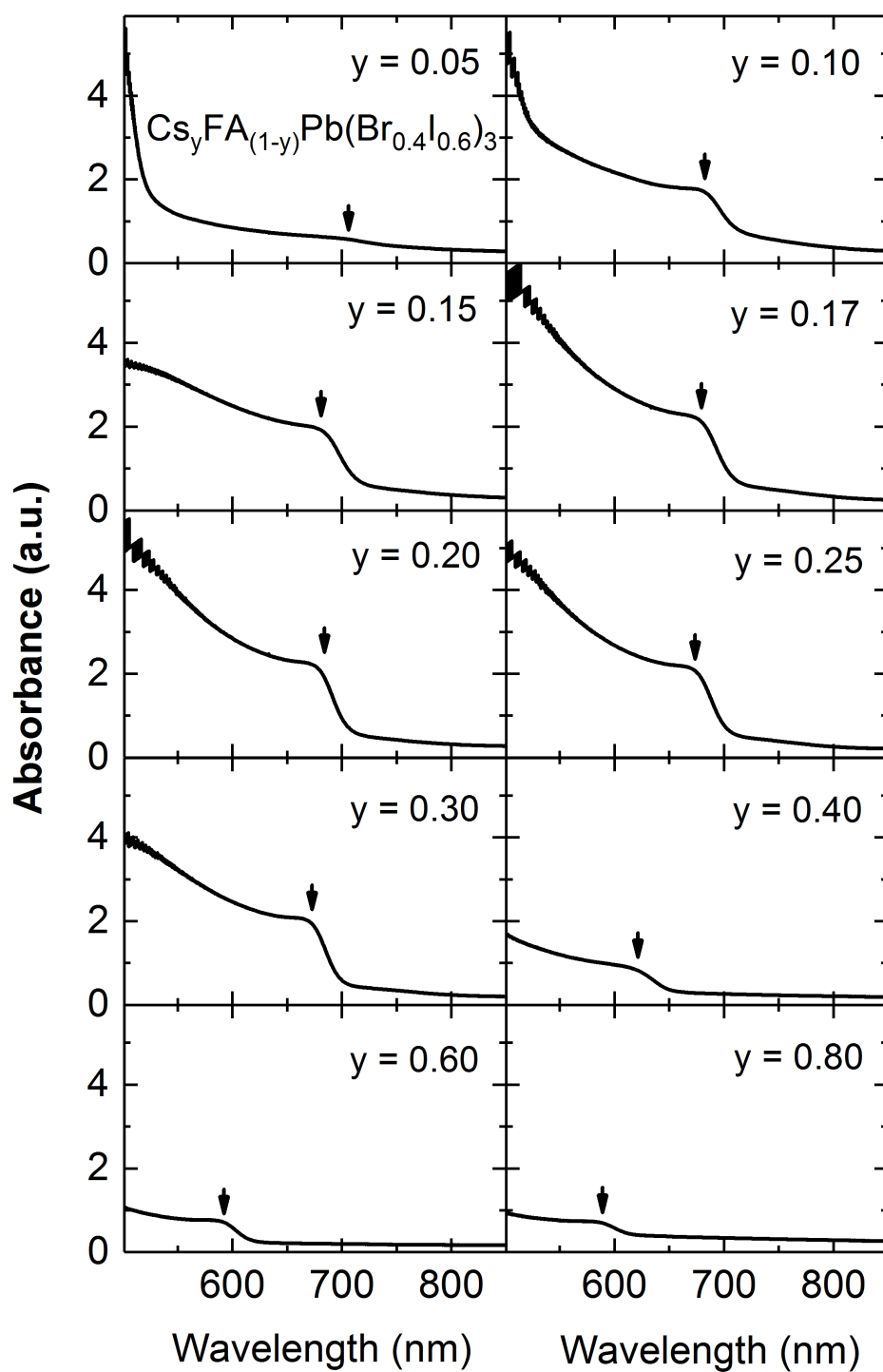


Figure 6.7: Absorbance spectra of $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ films with varying caesium content y . Vertical arrows indicate the absorption onsets. The data were obtained by measuring the optical transmission and reflection using a Fourier-transform infrared spectrometer.

duced microstrain, another indicator of high crystalline quality. To elucidate the link between crystalline quality and optoelectronic properties, the investigation is continued by determining charge-carrier mobilities and trap-related recombination rates in $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ films. Figure 6.8b presents effective charge-carrier mobilities measured using optical-pump, THz-probe (OPTP) spectroscopy. Under the reasonable assumption that excitonic effects are weak at room temperature [13, 131] and hence the free-charge conversion is close to unity, these values represent charge-carrier mobilities at THz frequencies. An excellent correlation between charge-carrier mobility and crystallinity is found (Figure 6.8a, b). Adding Cs to the poorly crystalline $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ film results in a steep rise in charge-carrier mobility up to a relative Cs content of 0.2 and is then followed by a plunge to much lower values in the $0.3 < y < 0.8$ region. Consequently, the material with the sharpest XRD diffraction peaks, $\text{Cs}_{0.2}\text{FA}_{0.8}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ ($y = 0.2$), also exhibits the highest charge-carrier mobility of $(18 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, consistent with a previous report for a similar composition [18], and signifying a striking improvement compared to the highly disordered FA cation, mixed-halide $\text{FAPb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskite ($1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) reported in Chapter 4.

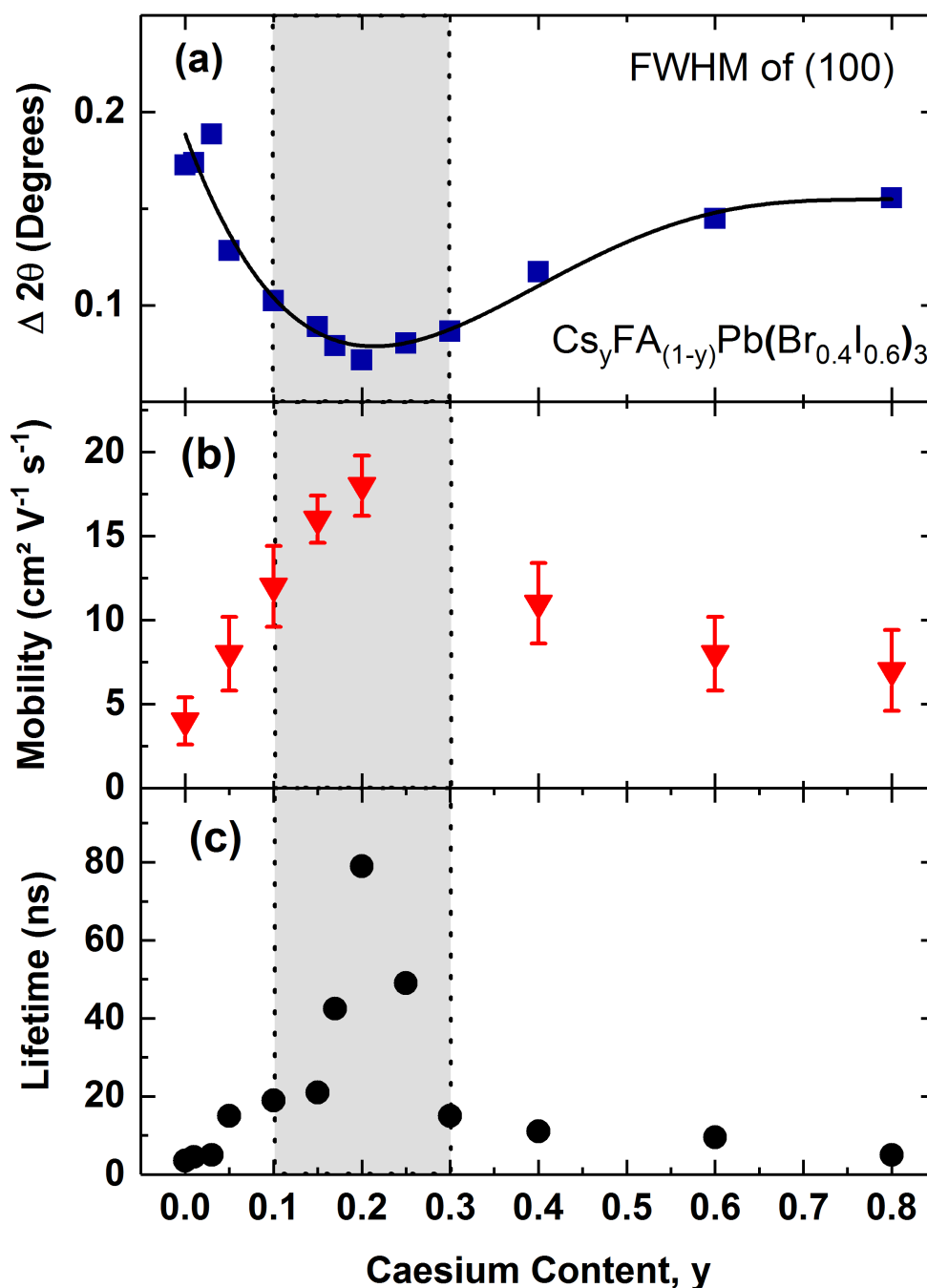


Figure 6.8: (a) Full width at half maximum (FWHM) of the (100) XRD peak in $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskites, with varying Cs content ($0.0 < y < 0.8$) taken from the respective XRD spectra (Figure A 7.1). The solid line is a guide to the eye. (b) Effective charge-carrier mobilities of $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ with varying Cs content y . Error bars indicate the range of values obtained. (c) Charge-carrier lifetimes of $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ films with varying Cs content obtained from TC-SPC measurements at low excitation fluence (Figure 6.9). The films were excited at a wavelength of 400 nm. The grey shaded area bound by dotted vertical lines marks the region of relative Cs content with high crystallinity and stability.

Another factor that may be strongly influenced by crystal grain size is trap-mediated recombination, considering that a number of studies suggest increased trap density at grain boundaries [106, 198]. According to DFT studies, such traps could comprise elemental defects such as lead vacancies (electron traps) or interstitial organic cation FA (hole traps) [199]. In addition, grain boundaries may reduce the bandgap and increase electron-phonon coupling, thus accelerating the non-radiative charge recombination [200]. Crystal defects, such as dislocations and terraces may also lead to microstrain in the perovskite and be responsible for the formation of trap sites [195]. Figure 6.8c displays time-resolved PL lifetimes derived from time-correlated single photon counting (TCSPC) (traces shown in Figure 6.9) under low-intensity pulsed excitation for which decay dynamics mostly reflect non-radiative trap-assisted recombination. PL lifetimes again inversely correlate with the XRD peak width, displaying a peak value for $y = 0.20$ (79 ns), with strongly diminishing numbers for compositions in the range of $y < 0.1$ (4 - 15 ns) and $y > 0.30$ (5 - 11 ns) (Figure 6.8c). For $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ hence the region of $0.1 < y < 0.3$ Cs content is identified as yielding the most stable crystal structure, highest crystalline quality and optimised optoelectronic properties for photovoltaics.

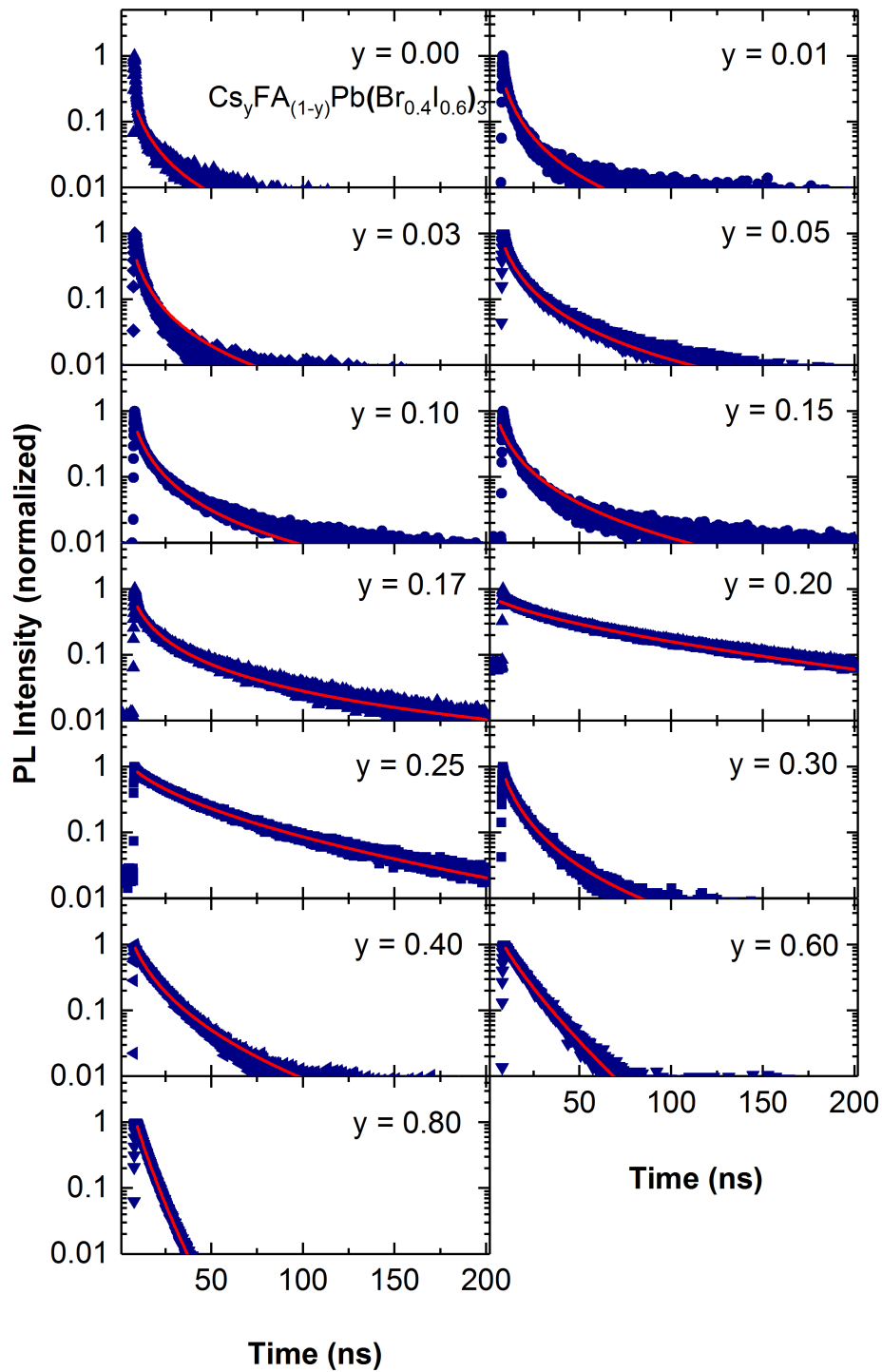


Figure 6.9: Time-resolved PL spectroscopy of $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ films with varying caesium content y , following excitation at 400 nm at an excitation fluence and $0.0151 \mu\text{J cm}^{-2}$. The laser intensity was at 2.53 W cm^{-2} . The PL decay traces have been normalised to the peak emission.

The crucial question to be answered for these mixed-halide perovskites is whether such systems can be stabilised against photo-induced halide segregation, which has been observed in a number of FA and MA based lead mixed halide perovskites [76, 93]. The light-induced mechanisms driving the segregation of such perovskites into iodide-rich and bromide-rich domains are still poorly understood. Therefore the now well-characterised $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ systems are used to investigate the photo-stability of the material against halide segregation and to explore the mechanisms driving this effect. In Figure 6.10 photoinduced changes to the PL emission wavelength as a function of time under excitation are shown for $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ films, using Cs concentration levels from three distinct regions of high FA ($y = 0.05$) and high Cs ($y = 0.60$) materials, and for the most crystalline material ($y = 0.20$). Over the course of 30 minutes the films are excited with light at 400 nm with an intensity of 100 mW cm^2 (equivalent 1 Sun), and the average energy of the emitted photons $\langle E_{\text{ph}} \rangle$ is extracted from the measured PL spectra (provided in Figure 6.11). It is found that the $\langle E_{\text{ph}} \rangle$ shows only a marginal change for the $y = 0.20$ film, while conversely, on the compositional edges, both the low Cs ($y = 0.05$) and high Cs ($y = 0.60$) films exhibit a decline in their average photon energy $\langle E_{\text{ph}} \rangle$ in accordance with halide segregation, which results in charge-carrier funnelling into low-bandgap iodide-rich domains.

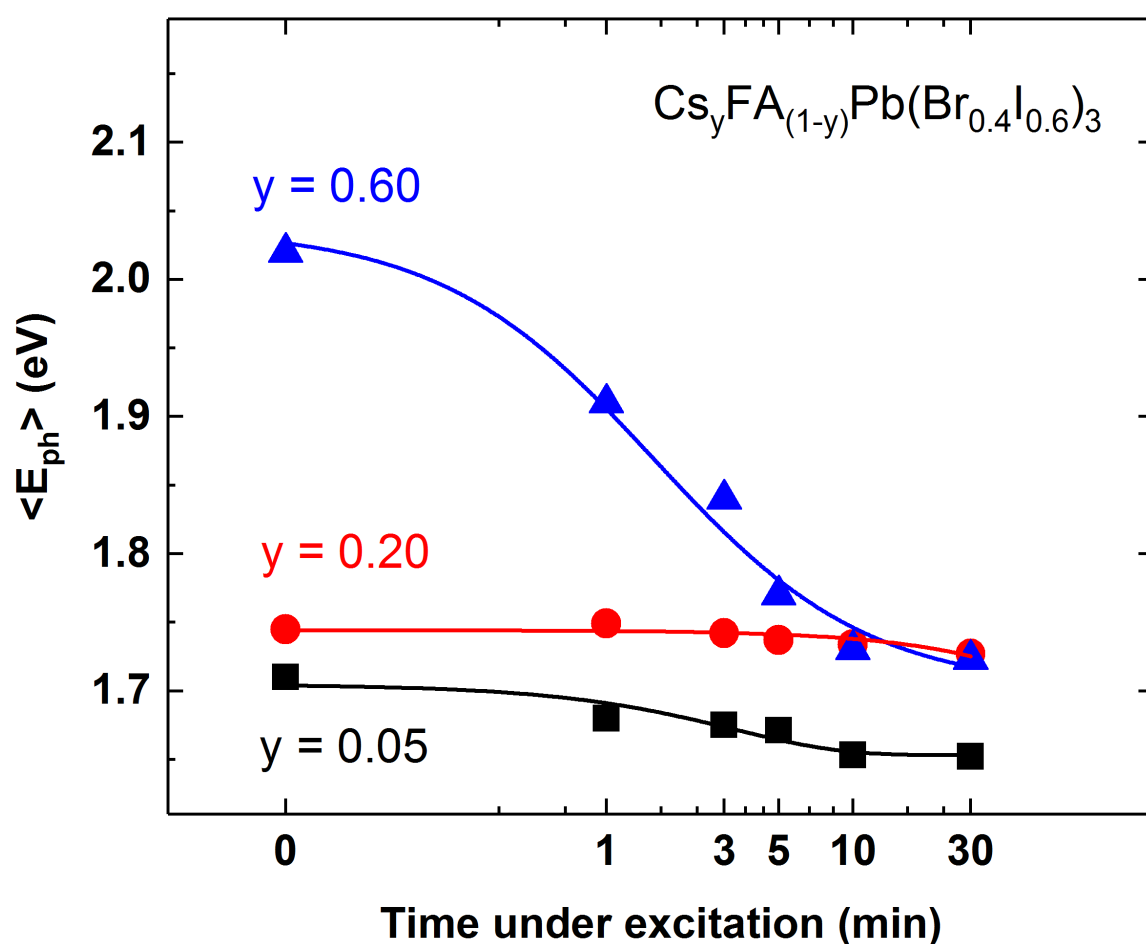


Figure 6.10: Change of the average PL photon energy $\langle E_{ph} \rangle$ for emission from three different $Cs_yFA_{(1-y)}Pb(Br_{0.4}I_{0.6})_3$ films with $y = 0.05$, $y = 0.20$ and $y = 0.60$. The films were exposed to continuous illumination over the course of 30 minutes and excited at 400 nm with an intensity of 100 mW cm^{-2} (fluence of $0.1 \text{ } \mu\text{J cm}^{-2}$, pulse duration 100 fs, repetition rate 80 MHz). Blue, red and black solid lines are guides to the eye. Inset: Spectral changes in emission from a $Cs_yFA_{(1-y)}Pb(Br_{0.4}I_{0.6})_3$ film over 30 minutes of continuous illumination.

These observations demonstrate a strong correlation between material crystalline quality and stability towards photo-induced halide segregation. It can be noted that Hu et al. similarly found that films of $\text{MAPbBr}_{0.8}\text{I}_{2.2}$ displayed strongly enhanced photo-stability when processed on a non-wetting hole transporting layer that yielded larger crystallites [96]. The obtained results hence demonstrate that the coveted scenario of stable mixed-halide perovskites with 1.7 to 1.8 eV band gap can be achieved provided the crystalline quality of the material is sufficiently high.

These findings also shed light on the fundamental mechanisms underlying the photo-induced halide segregation in mixed bromide-iodide perovskites. Recent theoretical work has suggested that the $\text{MAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ system suffers from a general miscibility gap in the central region ($0.3 < x < 0.6$) because of the mismatch between the two different halide anion radii [201]. However, photo-induced halide segregation in $\text{MAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ has been found to reverse spontaneously over the time scale of a few minutes after the illumination has been removed. Hence such experimental studies do not point towards a miscibility gap being primarily responsible for halide segregation, but rather towards a photo-induced, reversible migration of ions. The findings demonstrate that such photo-induced ion migration is aided in materials of low crystalline quality. There are two plausible explanations for why such correlation may occur. The first is that high material crystallinity and photo-stability against halide segregation simply derive from the same effect: that is, a perovskite crystal structure that lies well within the Goldschmidt tolerance factor provides high barriers against deterioration into both alternative crystal phases and halide segregation. However, consider this scenario unlikely as it cannot explain why one given mixed-halide perovskite can acquire higher photo-stability against halide segregation when it is processed into films of higher crystallinity [96]. Therefore a second alternative can be proposed as the more likely scenario, which is that regions of short-range crys-

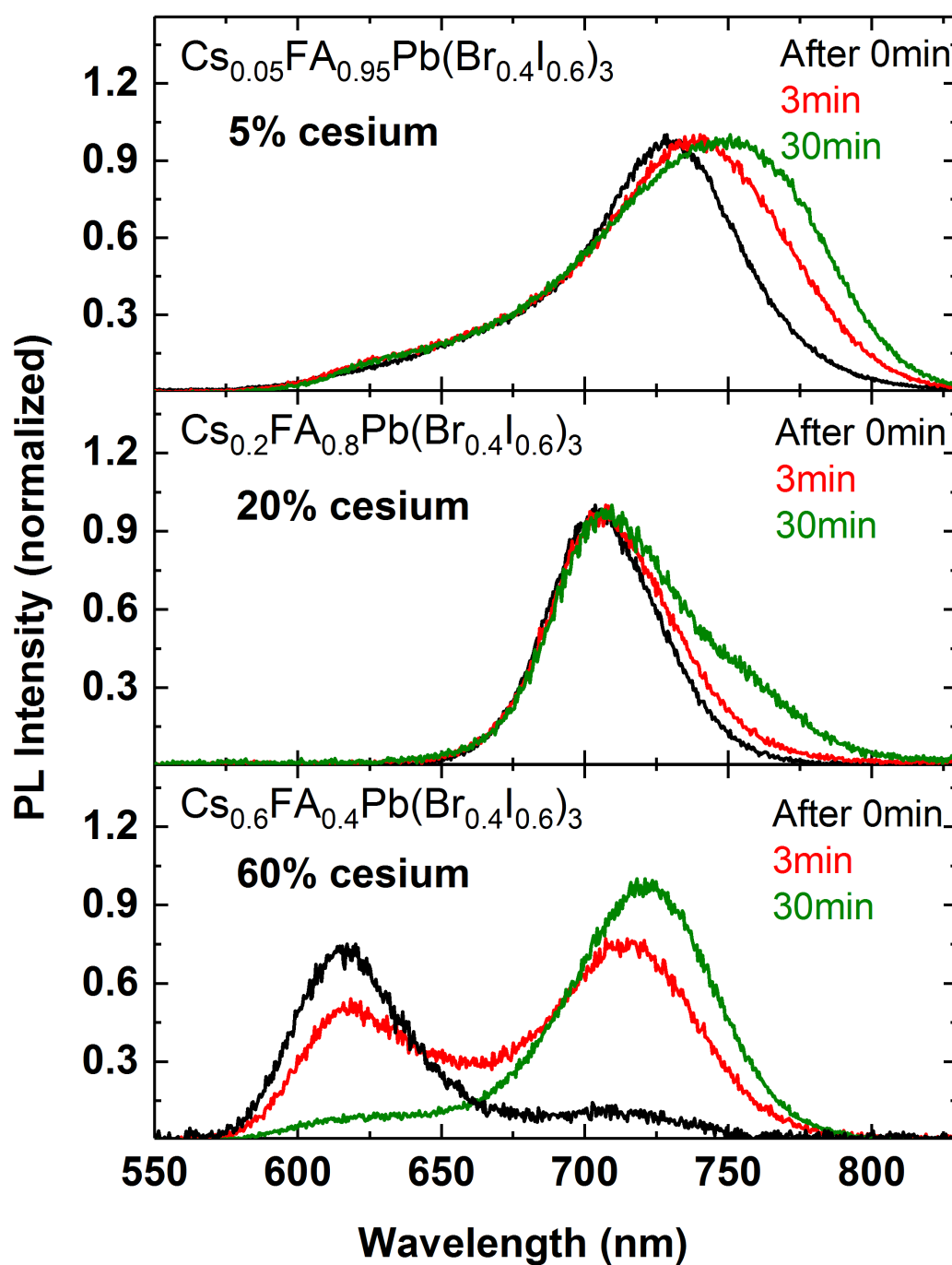


Figure 6.11: PL spectra of three different $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ films ($y = 0.05$, $y = 0.2$ and $y = 0.6$) over the course of 30 minutes of continuous illumination in vacuum following excitation at 400 nm at an intensity of 100 mW cm^{-2} (fluence of $0.1 \mu\text{J cm}^{-2}$, pulse duration 100 fs, repetition rate 80 MHz). The PL spectra have been normalised to the peak emission.

talline order aid the photo-induced segregation of mixed bromide-iodide perovskites. Such effects could for example derive from the large mismatch in lattice constant between iodide-rich and bromide-rich perovskites (see Figure 6.5a). Halide segregation within a single-crystal mixed-halide structure would cause sizeable lattice strain at the interfaces between iodide-rich and bromide-rich domains and may therefore not be energetically feasible. Near a grain boundary, or at the boundary between regions of short-range crystalline order, such lattice strain could be more easily accommodated without a penalty, facilitating halide segregation in materials of low crystallinity. An alternative possibility is that halide segregation is nucleated at already existing defect sites or amorphous regions which are present at grain surfaces in high density [106, 198]. Hence control over grain surfaces and crystallinity appear to be key to photo-stable mixed halide perovskites.

6.2.2 Optoelectronics of $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$

After establishing that highly crystalline $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ perovskites are feasible in the region of 20% Cs inclusion, the effect of varying halide composition is explored. Mixed lead halide perovskites $\text{APb}(\text{Br}_x\text{I}_{1-x})_3$ offer excellent band gap tunability that lends itself to light-emitting applications and optimised bandgap materials for tandem solar cells. While for a silicon-perovskite tandem a 30 - 40% Br perovskite top-subcell is required, alternative perovskite-perovskite tandem solar cells with MAPbI_3 require a top cell with higher than 60% Br fraction [193]. However, photo-stable tunability across the full bromide-iodide range has proven difficult for single-cation MA, FA or Cs perovskites, with crystallinity and charge-carrier mobility gaps appearing in the central region [76, 93]. Consequently, the optoelectronic prop-

erties of the $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ perovskite series with varying Br content x are unraveled.

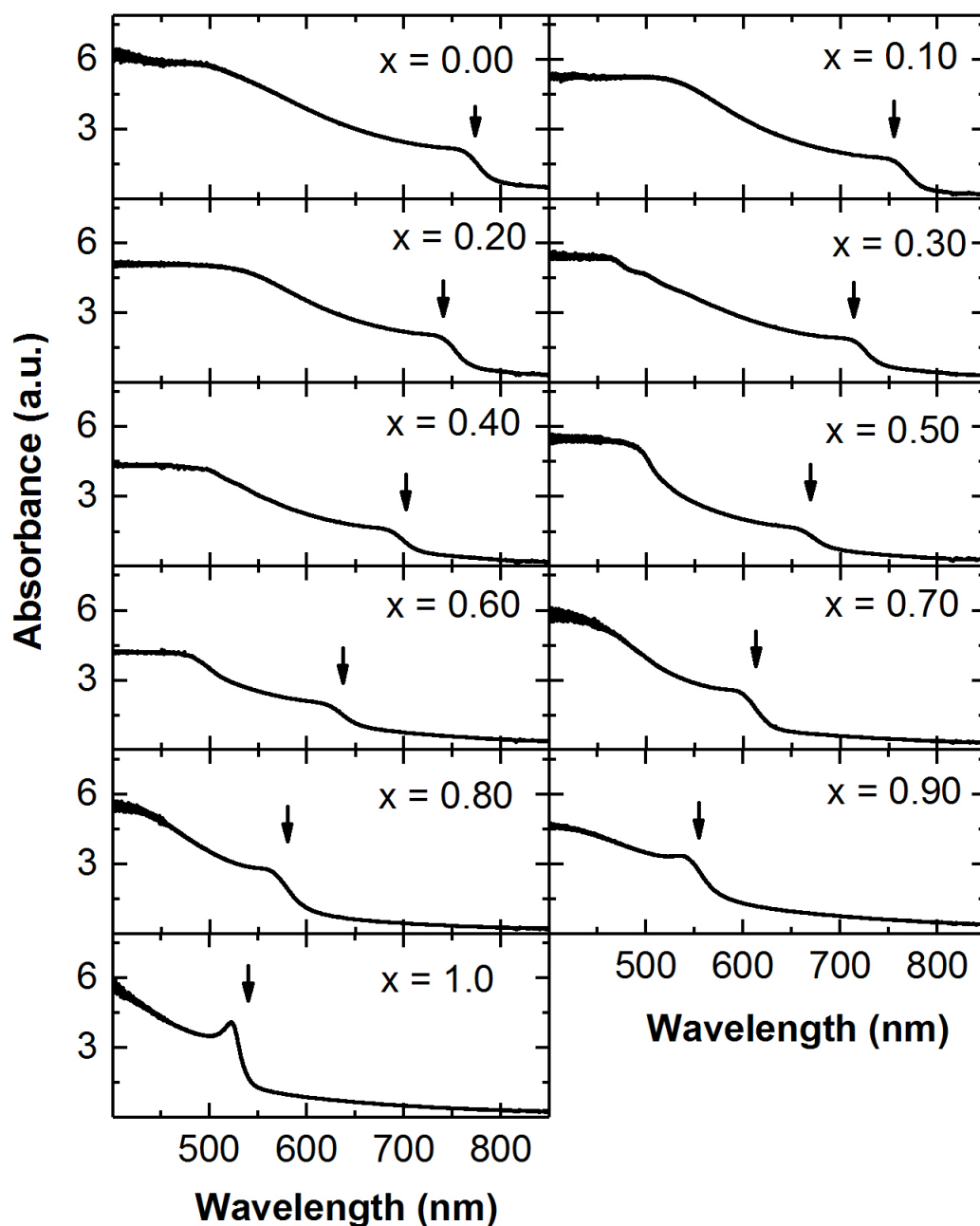


Figure 6.12: Absorbance spectra of $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ films with varying bromide content x . Vertical arrows indicate the absorption onsets. The data were obtained by measuring the optical transmission and reflection using a Fourier-transform infrared spectrometer.

First the trap-related monomolecular charge-carrier recombination channels by analysing the photoluminescence decay transients under low excitation fluences (Figure 6.13). From stretched exponential fits charge-carrier lifetimes τ across the series are extracted, which vary from 22 ns for 100% bromide to 191 ns for the 100% iodide film. Figure 6.14a displays the inverse value τ^{-1} , that is, the mono-molecular decay rates k_1 , as a function of bromide content for the whole series of 11 samples. Trap-related charge-carrier recombination increases monotonically with increasing bromide content, in particular beyond 60% bromide fraction. This effect most likely results from larger trap state densities in Br-rich films, which could again be related to lower crystallinity, in accordance with changes in charge-carrier mobility (vide infra). It has been proposed that for very high Br content, the thermodynamic favourability of the perovskite α -phase in Cs/FA lead mixed-halide perovskites may decrease [78] which could explain the observed trend. However, despite this, the stabilizing effect of Cs incorporation material series is a remarkable success, since it results in long charge-carrier recombination lifetimes in excess of several tens of nanoseconds even for the intermediate mixed-halide region ($0.3 < x < 0.5$), in marked contrast to FA-only perovskites investigated in Chapter 4 of this work.

Additionally, higher order recombination processes, such as bi-molecular (k_2) and Auger recombination (k_3) are examined, which typically only contribute significantly at charge-carrier densities in excess of 10^{18} cm^{-3} [131]. These rate constants are extracted from THz photoconductivity transients obtained from ultrafast optical-pump THz-probe spectroscopy (Figure 6.15) which reflect the decay of charge-carriers following photo-excitation with an intense pulse at 400 nm. Fits of the solutions to the rate equation $dn(t)/dt = -k_3n^3 - k_2n^2 - k_1n$, modified to account for the excitation density profile yield bi-molecular (k_2) and Auger recombination (k_3) rate constants (see Chapter 3.1.5 for details) as a function of bromide fraction, as shown in Figure 6.14. In excellent agreement with the study presented in Chapter 4, it is found that increasing the bromide fraction from 0 to 1 leads to an increase by roughly an order of magnitude for both k_2 ($0.1 - 2.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) and k_3 ($0.1 - 0.8 \times 10^{-28} \text{ cm}^6 \text{ s}^{-1}$). Such correlations confirm that these processes are intrinsic to band structure changes encountered across the series, rather than crystallinity or disorder.

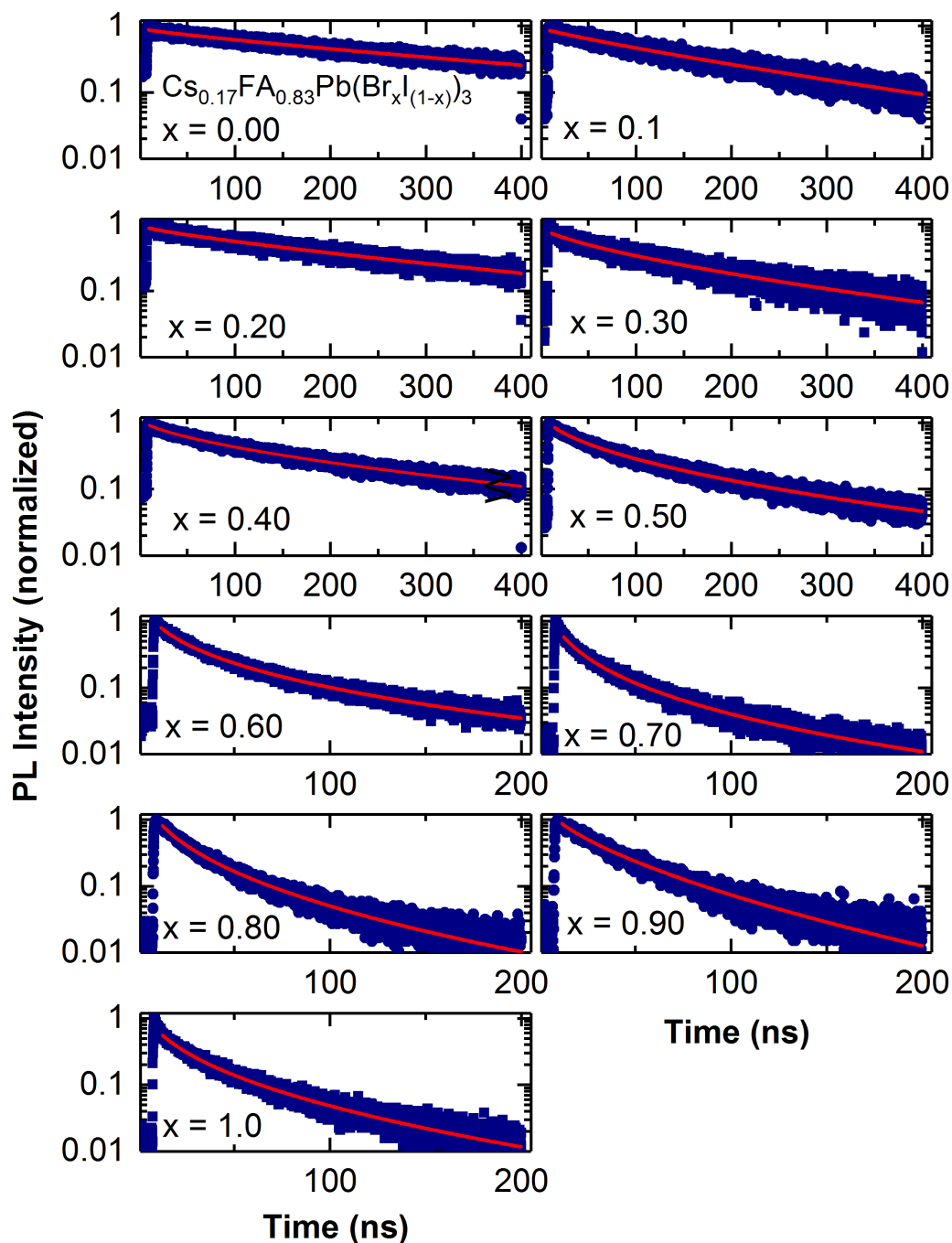


Figure 6.13: Time-resolved PL spectroscopy of mixed-halide $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ films with varying bromide content x , following excitation at 400 nm at a low excitation fluence of $0.015 \mu\text{J cm}^{-2}$. The laser intensity was at 2.53 W cm^{-2} . The PL decay traces have been normalised to the peak emission.

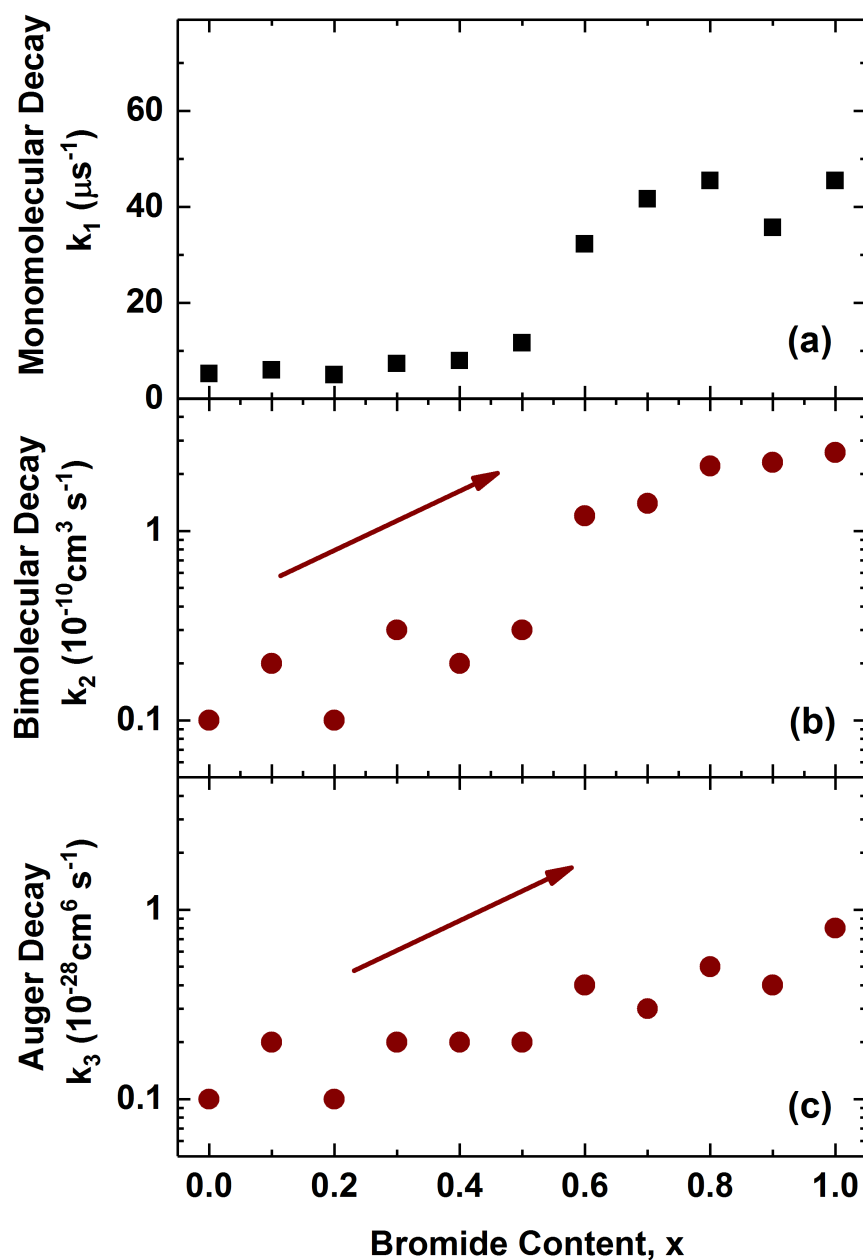


Figure 6.14: (a) Mono-molecular, (b) bi-molecular and (c) Auger recombination rate constants, k_1 , k_2 and k_3 for mixed-halide $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites with varying Br content x . Values for k_1 were extracted from stretched exponential fits to PL decay traces from time-resolved PL measurements. The inset to (a) shows an example PL decay trace for the iodide-only mixed cation $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_3$ film, including a stretched exponential fit (red line). Values for k_2 and k_3 were extracted from fits to THz photoconductivity transients which are shown in Figure 6.15.

Finally, the charge-carrier scattering mechanisms in $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ are investigated which may be probed by measurements of the PL linewidth and charge-carrier mobility across the series. Across the full range from 100% iodide ($x = 0$) to 100% bromide ($x = 1$) the FWHM of the PL spectra (Figure 6.16) exhibit a continuous increase up until $x < 0.8$ beyond which a slight decrease is recorded (Figure 6.17a). Two factors are likely to influence the observed trends here. On the one hand, lowered crystallinity and disordered alloy formation are associated with higher energetic disorder, which yields broader PL spectra. This effect has been observed through correlations between the FWHM and the Urbach energy associated with absorption tails [125], and with charge-carrier mobility (see Chapter 4.3). Such disorder may be more prevalent for the central region where even bromide-iodide content supports higher alloying disorder [201], and towards higher bromide fraction because of the slightly decreased thermodynamic favourability of perovskite α -phases in Br-rich films [78]. In addition to these extrinsic, disorder-related effects, intrinsic factors such as changes in electron-phonon coupling can influence PL line shape broadening and charge-carrier mobilities [202]. It has recently been shown that FAPbBr_3 supports stronger electron-phonon coupling via a dominant Froehlich interaction of charge-carriers with LO phonons than FAPbI_3 because the former is associated with a smaller value of the high-frequency dielectric function [202]. Hence the increase in electron-phonon interactions can contribute to the trend of increasing PL broadening with increasing bromide content.

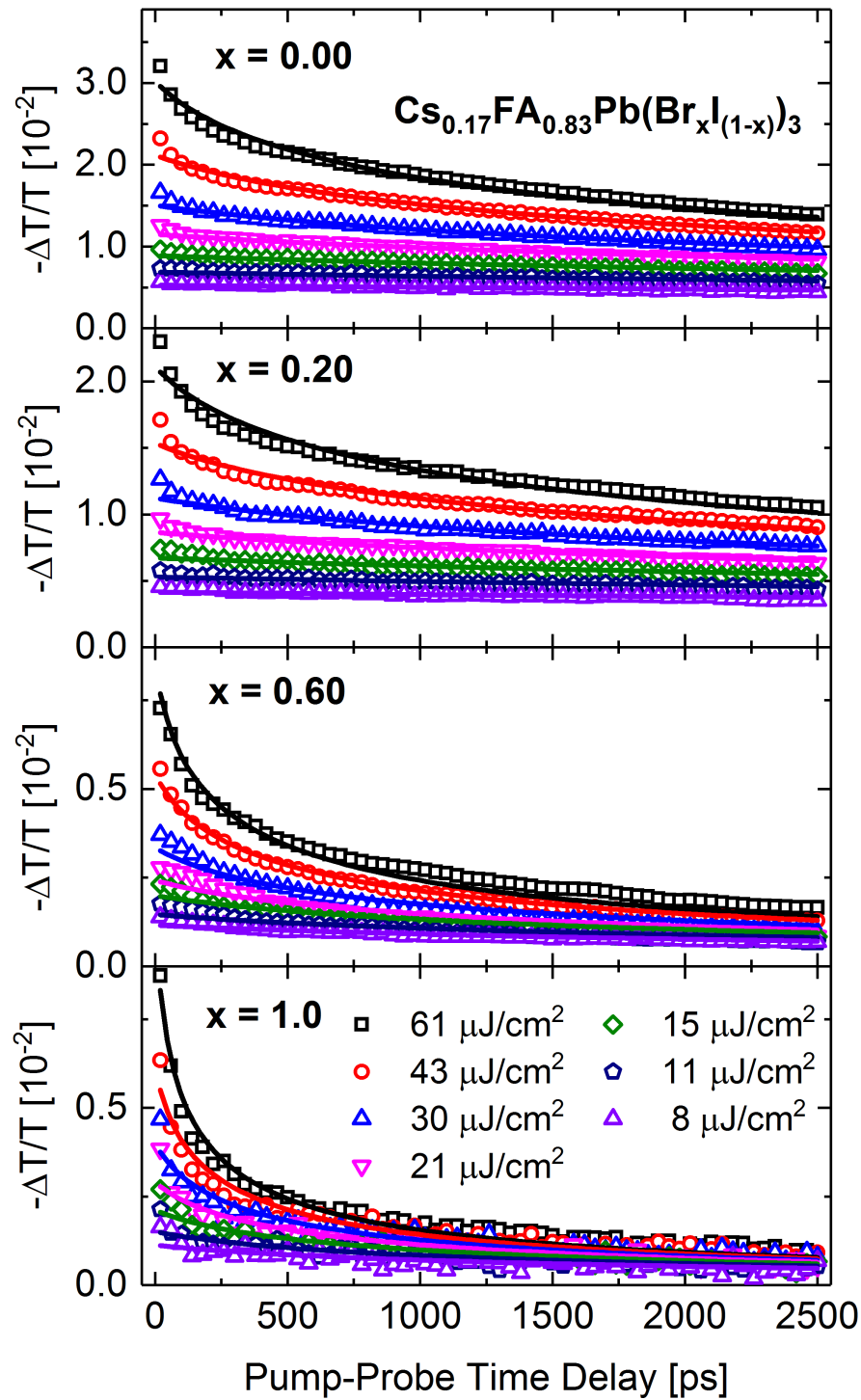


Figure 6.15: THz photoconductivity transients in thin films of $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ with a) $x = 0.0$, b) $x = 0.20$, c) $x = 0.60$ and d) $x = 1$, for excitation fluences between $8 \mu\text{J cm}^{-2}$ and $61 \mu\text{J cm}^{-2}$ at an excitation wavelength of 400nm. The symbols represent data points, and the solid lines are fits.

Charge-carrier scattering caused by extrinsic disorder or intrinsic interactions with phonons will also adversely affect the charge-carrier mobility.

To further investigate such effects, in Figure 6.17b charge-carrier mobility values as a function of Br content are displayed, as extracted from THz photo-conductivity measurements (see Chapter 3.1.5 for details). A continuous decrease of the mobility with increasing Br content is found, which is in accordance with the increase in charge-carrier scattering already evident in the PL emission linewidth. Hence the highest charge-carrier mobility values are found for iodide-rich films ($0 < x < 0.2$), and reach excellent values between $34 - 40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The presence of 17% caesium in $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_3$ thus increases the charge-carrier mobility by almost 50% with respect to FAPbI_3 for which a THz mobility of $27 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported in Chapter 4.3. Importantly, caesium clearly stabilises the charge-carrier mobilities in the intermediate mixed-halide regime ($0.3 < x < 0.5$) where values for $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ now range between $15 - 24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, in contrast to the $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported in Chapter 4.3 for $\text{FAPbBr}_{0.4}\text{I}_{0.6}$. The addition of caesium hence leads to a stabilization of the crystal structure against both structural changes and halide segregation that is in turn reflected in drastically improved charge-carrier motion through the perovskite. High charge-carrier mobilities within the active layer are crucial for charge-carrier extraction from the complete photovoltaic cell. To illustrate this point, Figure 6.17b also displays charge-carrier diffusion lengths L_D calculated from the Einstein relation using the determined charge-carrier recombination constants (k_1 , k_2 , k_3) and mobilities (Figure 6.18). At a charge-carrier density typical for photovoltaic device operation ($n = 10^{15} \text{ cm}^{-3}$), charge-carrier diffusion lengths are found in the micron range tuning monotonically from $0.8 \text{ }\mu\text{m}$ for $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbBr}_3$ to $4.4 \text{ }\mu\text{m}$ for $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_3$ without any sign of the disorder and instability gap previously observed for the FA-only system. In addition, all values significantly exceed the optical absorption depth,

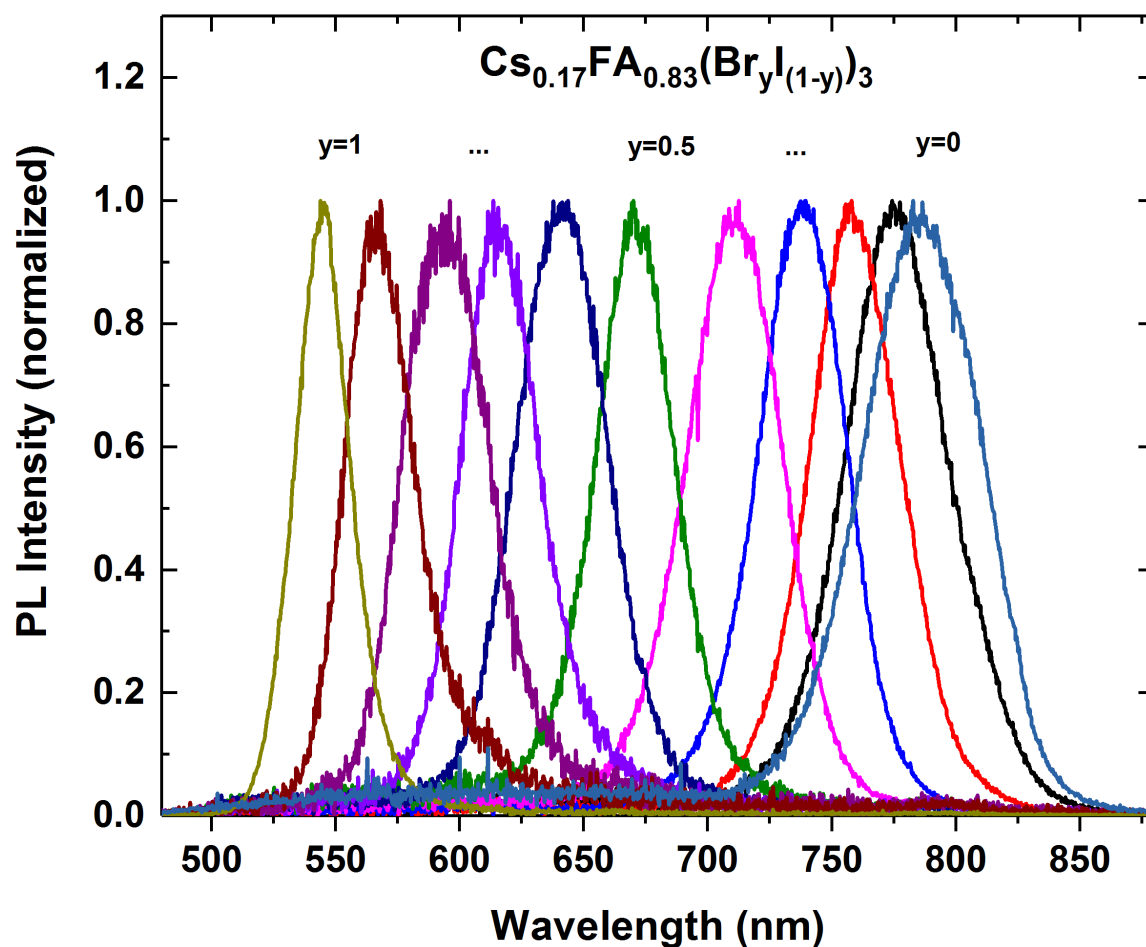


Figure 6.16: Steady-state photoluminescence (PL) spectra of $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ thin films with varying bromide content x , recorded immediately following excitation at 400 nm at a fluence of $13.5 \mu\text{J cm}^{-2}$ (14.9 mW cm^{-2}) under vacuum. The PL spectra have been normalised to the peak emission.

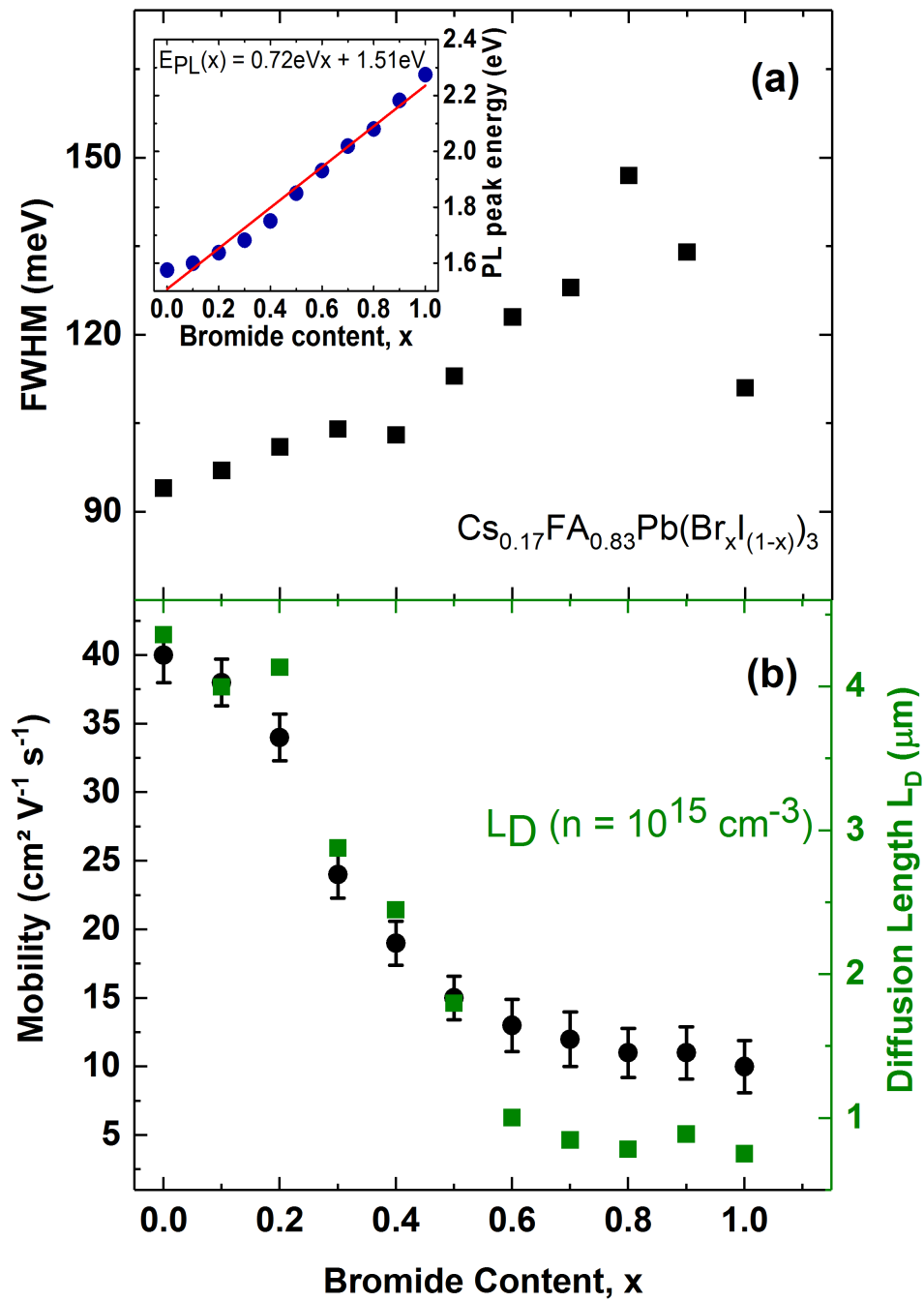


Figure 6.17: (a) FWHM of the PL emission spectra of mixed-halide $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ perovskites as function of Br content x . Inset: Correlation of the PL peak energy with changing Br content. The red solid line is a linear fit yielding $E_{\text{PL}}(x) = 0.72 \text{ eV}x + 1.51 \text{ eV}$. (b) Effective charge-carrier mobilities (black dots) and charge-carrier diffusion length (green squares) of mixed-halide $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$ with varying Br content. Error bars indicate the range of values obtained.

demonstrating that mixed-halide perovskites can clearly serve as materials in efficient planar-heterojunction solar cells across the full halide tuning range thus enabling a variety of tandem combinations.

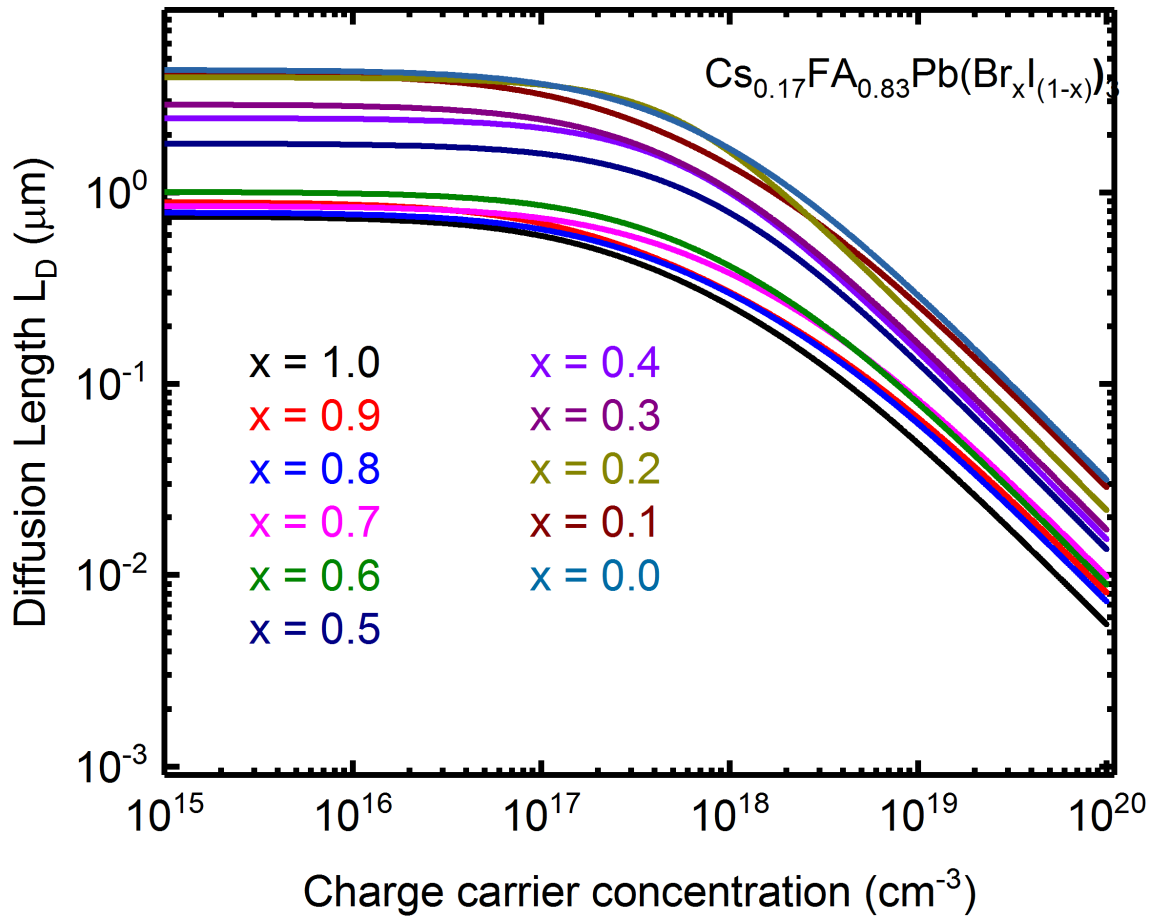


Figure 6.18: Charge-carrier diffusion lengths as a function of charge-carrier concentration in $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ thin films with varying bromide content x .

6.2.3 Conclusions

In summary, pertinent links between crystal phase stability, photo-stability and optoelectronic properties in mixed-cation lead mixed-halide $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ perovskite films have been revealed. By finely tuning the Cs content y in the perovskite, a stable region between $0.10 < y < 0.30$ of high crystalline quality, high photo-stability against halide segregation and excellent charge-carrier lifetimes and mobilities has been ascertained. Within this stable region, the effective cation radius of the FA/Cs mixture is located well within the Goldschmidt tolerance factor and hence stable formation of a perovskite α -phase is preferred over deterioration into a photo-inactive yellow non-perovskite γ -phase. Within the $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ series, optimised optoelectronic properties for $y = 0.20$ are found, which exhibits high charge-carrier mobilities of $(18 \pm 2) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and charge-carrier lifetimes of 80 ns. Importantly, it could effectively be demonstrated that for materials with high crystallinity, photo-induced halide segregation is strongly suppressed. It can be proposed that regions of short-range crystalline order, or grain boundaries, enable halide segregation, possibly by releasing lattice strain between iodide rich and bromide rich domains, or by providing nucleation sites through defects or amorphous material accumulated near grain boundaries. Such correlations also suggest that the stoichiometry of the perovskite alone may not be the only factor determining photo-stability. For example, even within the parameter space explored here, changes in processing conditions or ambient moisture could erode crystallinity, making these same materials susceptible to photo-induced halide segregation. In addition, it can be postulated that the A-cation segregation could also trigger halide segregation; a normally stable material with stoichiometry $\text{Cs}_{0.2}\text{FA}_{0.8}\text{Pb}(\text{Br}_{0.4}\text{I}_{0.6})_3$ could still fall outside of the stability zone normally attained for 10 - 30% Cs if it was actually composed of segregated domains with 0% (FA only) and 40% Cs, each of which falls outside the stable range. These

examples highlight that in order to attain materials that are photo-stable against halide segregation, processing routes must yield large grain sizes and even alloying. As shown here, these targets are highly feasible. Finally, the orthogonal halide-variation parameter space for $\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ perovskites over the full compositional range ($0 < x < 1$) is explored. It has been demonstrated that once the material contains a sufficient fraction of caesium, excellent charge-carrier mobilities and diffusion lengths can be obtained across the full bromide-iodide tuning range. Band gaps tune linearly with Vegard’s law across the whole range, and unlike previously observed for $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$, there are no effects of lowered optoelectronic properties or stability in the central region. Therefore, the addition of some caesium yields an otherwise elusive perovskite system whose absorption onsets can be tuned for optimised, photo-stable perovskite-perovskite and silicon-perovskite tandem solar cells.

Chapter 7

Conclusions and Outlook

Since the first proof of concept demonstration of a metal-halide perovskite absorber layer employed in a solar cell device by Kojima et al., research on photovoltaic perovskite materials has been striding ahead in an unmatched pace compared to any other emerging thin-film photovoltaic technology. One of the most striking aspects of metal-halide perovskites is the ABX_3 crystal structure, which is unique in the sense that it enables a wide tunability of bandgap by simply intermixing structural components, thus opening up possibilities for highly efficient tandem solar cell designs and colour variation. Although, this advantage makes perovskites an extraordinary class of versatile photovoltaic absorbers from amongst the entire portfolio of available photovoltaic technologies, it is of utmost significance to unravel in which way their tunability is expedient for controlling other photovoltaic parameters and properties, such as charge-carrier dynamics and mobilities. Taking this context as the starting point of the work presented in this thesis, the following paragraphs present an overview of the scientific progress made, pitfalls discovered and critical reflections on future opportunities and pathways in this special area of research.

To begin with, $\text{FAPb}(\text{Br}_y\text{I}_{(1-x)})_3$ mixed-halide perovskites were examined as the most attractive perovskite compound offering tunability across the entire visible spectrum via compositional variation and a better thermal stability compared to its MA-based counterpart. Charge-carrier dynamics investigations carried out by transient optical pump - THz probe spectroscopy yielded strongly non-Langevin bimolecular and Auger charge-carrier recombination rate constants, thus projecting the predominance of efficient charge-carrier extraction over recombination mechanisms across the entire compositional range.

Besides, charge-carrier recombination rates were found to correlate with the bromide-iodide fraction x , which incidentally happens to be an order of magnitude lower for FAPbI_3 compared to the lighter halide FAPbBr_3 . The obtained results suggest an inherent dependence of charge-carrier dynamics with electronic structure and halide frontier orbital composition, which is the first such report for tunable lead mixed-halide perovskites.

On the other hand, charge-carrier mobilities across the bromide-iodide tuning range correlate with the crystallinity of the material rather than the electronic structure. At compositional edges, FAPbBr_3 and FAPbI_3 bring about charge-carrier mobilities of 14 and 27 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, whereas in between the values fall off, even to the point where they only reach $<2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for the intermediate region between $x = 0.3$ and $x = 0.5$, as evidenced by enhanced energetic disorder and trap-induced recombination here. Such low mobilities typically suggest heavily increased charge-carrier scattering at grain boundaries. It is commonly accepted, that grain boundaries are preferred routes for ion migration [203] and most likely act as barriers for electrons, which restrict their intra-crystallite movements and thus reduce their long-range mobilities [204].

Besides, fundamental issues have been observed regarding the photo-stability of mixed-halide perovskite absorbers. Exposing bromide-rich films to continuous light illumin-

ation effectuates photoinduced halide-segregation with shifts to lower energies arising from the formation of iodide-rich domains at lower bandgap regions. Earlier concerns of this effect cutting down photovoltaic performance have indeed been confirmed, stressing the urgency this matter has to be dealt with for ensuring long-term applicability of mixed-halide perovskites in photovoltaic devices [205].

The problematic crystal phase transition between $x = 0.3$ and $x = 0.5$ affects the 1.7 eV bandgap region, which is considered important for making a perovskite top-subcell in a perovskite-silicon tandem solar cell design. The strive after a perovskite composition that remains structurally stable in this region led over to an attempt of achieving this via targeted compositional engineering of the A-site cation that shall not only reduce the level of octahedral tilting-induced distortion in the lattice, but also push the bandgap to this desired bandgap.

Strikingly, a partial substitution of FA for the inorganic and more stable caesium, proved sufficient enough to fabricate a highly crystalline mixed-cation lead mixed-halide perovskite film with a band gap of 1.74 eV. The $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite exhibited sharp optical band edges and suppressed halide-segregation of the PL following continuous-wave laser irradiation at 5 W cm^{-2} , completely. Besides, the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ film yielded an excellent charge-carrier mobility of $21 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. For comparison, the corresponding neat FA perovskite $\text{FAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ only reached a value of $<1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in conformity with the highly non-crystalline ('amorphous') and energetically disordered structure found for this particular composition located in the phase transition region between $x = 0.3$ and $x = 0.5$.

This comparison clearly confirms that enhancing the crystallinity across a wider range of Cs/FA mixed-cation compositions is an adequate route to improve optoelectronic properties and stability of perovskite materials. This stands in agreement with charge-

carrier mobilities measured for mixed-cation $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$ films shown in Chapter 5.2.4, which increased monotonically with crystal grain sizes and only levelled off once the grains surpassed an assumed ‘threshold size’ beyond which scattering off grain boundaries became insignificant [102]. In order to extend the scope of this work, elaborating transitions and boundaries of structurally stable compositional regions which lack the detrimental impositions of non-benign grain boundaries and photo-induced halide-segregation would be the most recommendable move.

Hence, in a final step, the large orthogonal parameter space of $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ perovskites was explored to establish crucial links between crystal phase stability, photostability and optoelectronic properties. The caesium content region between $0.10 < y < 0.30$ was found to feature high crystalline quality, high charge-carrier mobilities and long charge-carrier lifetimes exceeding carrier transit time through the thin films.

Again, these high-quality perovskites demonstrate how photo-induced halide segregation is strongly suppressed, suggesting that high crystalline quality is a prerequisite for good optoelectronic quality and band gap stability. Regions of short-range crystalline order facilitate halide-segregation by releasing lattice strain between iodide rich and bromide rich domains. Nonetheless, the question remains whether simply observing stable PL energy over time is sufficient to make photo-stability claims. The marked improvements in terms of photostability could partly also derive from morphology-induced enhancements rather than deriving only from A-site cation intermixing. For future investigations, a concurrent control of film morphology and other confluencing factors mentioned in Chapter 2.5.4 is strongly advised [99] as this would enable pinpointing the mechanisms and root causes responsible for this effect more accurately.

For an optimised caesium content, the orthogonal halide-variation parameter space brought about charge-carrier mobilities in the range of $11 - 40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and diffusion lengths of $0.8 - 4.4 \text{ }\mu\text{m}$. Hence, from the results obtained, it can be stated that an inclusion of 17% caesium leads to an increase of charge-carrier mobility of up to 50% when transitioning the single-cation tri-halide perovskite ($27 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) to the equivalent Cs/FA mixed-cation perovskite ($40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Although, these are one of the highest mobilities ever reported for any polycrystalline hybrid perovskite material extracted from transient THz spectroscopy [102], the degree of improvements do not seem to be proportional to the drastic improvement achieved with respect to crystallinity. Furthermore, they did not bring about charge-carrier mobilities that are competitive with those of inorganic semiconductors (e.g. GaAs), where electron mobilities are found in the thousands of $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Even single-crystal perovskites - despite remarkable material purity - barely reach charge transport properties known for inorganic semiconductors [102], which corroborates the intrinsic limitations of perovskite materials (mainly electron-phonon coupling) thoroughly discussed in chapter 2.6. Also, in this work, the frequency-domain THz photoconductivity spectra taken for single-cation FAPbBr_3 perovskite shows Drude-like patterns (Figure 4.4), which suggests that there was no significant limitation by charge-carrier scattering off grain boundaries. Future improvements could thus be rather expected from material processing, film fabrication and structural stabilisation with the aim of reducing further hazards for charge-carriers, such as nonradiative trapping. The iodide-rich fractions of the mixed-cation perovskites examined in Chapter 6.2 already yield low monomolecular recombination rates in the range of $<10 \text{ }\mu\text{s}^{-1}$, which is leading the way to the right direction for thin-film optimisation.

By and large, it can be inferred that charge-carrier mobilities achieved for both the single-cation $\text{FAPb}(\text{Br}_x\text{I}_{(1-x)})_3$ and mixed-cation $\text{Cs}_y\text{FA}_{(1-y)}\text{Pb}(\text{Br}_x\text{I}_{(1-x)})_3$ series are

still more than sufficient for charge-carriers to diffuse through the material given the favourably slow recombination dynamics. With diffusion lengths in the micrometer range for many of the key material compositions investigated in this work, their utilization in photovoltaic devices outside the research lab seems indispensable, though further path-breaking improvements in terms operational stability remain subject to long-term structural and ambient stability.

Stability aspects represent the most ardent of challenges and the very prerequisite for perovskites to become a state-of-the-art and marketable solar energy technology. The breakthroughs achieved in this work can essentially be traced back to structural stabilisation achieved via A-site cation mixing of Cs and FA. It has been argued, that for a structurally stable region, the FA/Cs mixture is located well within the Goldschmidt tolerance factor, which is currently the most widely used predictor of perovskite stability. However, a growing number of reports suggest a revision of the ionic Shannon radii for cations that such predictions heavily rely upon [206]. Some important metal-halide perovskites show increased covalency in metal-halide bonds compared to metal-oxide or fluoride bonds earlier used to calculate Shannon radii [206]. Adaptations in this regard could help in rectifying stability predictions for known elements already used in metal-halide perovskites and also justify the addition of new contenders.

Bibliography

- [1] International Energy Agency. Tracking Clean Energy Progress. France: IEA Publications, **2017**.
- [2] Harry Wirth. Recent Facts about Photovoltaics in Germany. Germany: Fraunhofer ISE, **2017**.
- [3] M. A. Green. Third generation photovoltaics: solar cells for 2020 and beyond. *Physica E*, **2002**, 14, 65-70.
- [4] M. Graetzel. Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells. *Inorg. Chem.*, **2005**, 44, 6841-6851.
- [5] M. Graetzel. Recent Advances in Sensitized Mesoscopic Solar Cells, *Acc. Chem. Res.*, **2009**, 42, 1788-1798.
- [6] http://www.nrel.gov/ncpv/images/efficiency_chart.jpg
(Accessed 19/07/2017)
- [7] N.-G. Park, M. Graetzel, T. Miyasaka, K. Zhu and K. Emery. Towards stable and commercially available perovskite solar cells. *Nat. Energy*, **2016**, 1, 16152.
- [8] C. C. Stoumpos, C. D. Malliakas and M. G. Kanatzidis. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties. *Inorg. Chem.*, **2013**, 52, 9019-9038.

- [9] C. Wehrenfennig. Ultrafast Spectroscopy of Charge Separation, Transport and Recombination Processes in Functional Materials for Thin-Film Photovoltaics. PhD thesis, University of Oxford, **2014**.
- [10] N. Pellet, P. Gao, G. Gregori, T. Yang, M. K. Nazeeruddin, J. Maier and M. Graetzel. Mixed-Organic-Cation Perovskite Photovoltaics for Enhanced Solar-Light Harvesting, *Angew. Chem. International Edt.*, **2014**, 53, 3151-3157.
- [11] H. J. Snaith. Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells. *J. Phys. Chem. Lett.*, **2013**, 4, 3623-3630.
- [12] M. Johansson and P. Lemmens. Crystallography and Chemistry of Perovskites. *In Handbook of Magnetism and Advanced Magnetic Materials*, **2007**.
- [13] L. M. Herz. Charge-Carrier Dynamics in Organic-Inorganic Metal Halide Perovskites. *Annu. Rev. Phys. Chem.*, **2016**, 67, 65-89.
- [14] R. I. Hines, N. L. Allan and Wendy R. Flavell. Oxidation catalysts: a comparative simulation study of the lattice, defect and surface structure of the stannates ASnO_3 ($A = \text{Ca}, \text{Sr}$ and Ba) and SnO_2 . *J. Chem. Soc.*, **1996**, 92, 2057-2063.
- [15] A. M. Glazer. The classification of tilted octahedra in perovskites. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, **1972**, 28, 3384-3391.
- [16] V. M. Goldschmidt. Die Gesetze der Krystallochemie. *Naturwissenschaften*, **1926**, 21, 477-485.
- [17] H. D. Kim, H. Ohkita, H. Benten and S. Ito. Photovoltaic performance of perovskite solar cells with different grain sizes. *Adv. Mater.*, **2015**, 28, 917-922.
- [18] G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz and H. J.

- Snaith. Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells. *Energy Environ. Sci.*, **2014**, 7, 982-988.
- [19] N.-G. Park. Perovskite solar cells: an emerging photovoltaic technology. *Mater. Today*, **2015**, 18, 65-72.
- [20] J.G. Bednorz and K.A. Mueller. $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$: An XY Quantum Ferroelectric with Transition to Randomness. *Phys. Rev. Lett.*, **1984**, 52, 2289.
- [21] J. G. Bednorz and K. A. Mueller. *Phys. B: Condens. Matter*, **1986**, 64, 189-193.
- [22] T. Ishihara. Optical properties of PbI-based perovskite structures. *J. Lumin.*, **1994**, 60-61, 269-274.
- [23] D. B. Mitzi, C. A. Feild, W. T. A. Harrison and A. M. Guloy. Conducting tin halides with a layered organic-based perovskite structure, *Nature*, **1994**, 369, 467-469.
- [24] D. B. Mitzi, S. Wang, C. A. Feild, C. A. Chess, A. M. Guloy, *Science*, **1995**, 267, 1473-1476.
- [25] K. Chondroudis and D. B. Mitzi. Electroluminescence from an organic-inorganic perovskite incorporating a quaterthiophene dye within lead halide perovskite layers. *Chem. Mater.*, **1999**, 11, 3028-3030.
- [26] C. R. Kagan, D. B. Mitzi and C. D. Dimitrakopoulos. Organic-inorganic hybrid materials as semiconducting channels in thin-film field-effect transistors. *Science*, **1999**, 286, 945-947.
- [27] K. Tanaka, T. Takahashi, T. Kondo, K. Umeda, K. Ema, T. Umebayashi, K. Asai, K. Uchida and N. Miura. Electronic and excitonic structures of inorganic-organic perovskite-type quantum-well crystal $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$. *Jpn. J. Appl. Phys.*, **2005**, 44, 5923-5932.

-
- [28] A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.*, **2009**, 131, 6050-6051.
- [29] J. H. Im, C. R. Lee, J. W. Lee, S. W. Park and N. G. Park. 6.5% efficient perovskite quantum-dot-sensitized solar cell. *Nanoscale*, **2011**, 3, 4088.
- [30] H. Kim, C. Lee, J. Im, K. Lee, T. Moehl, A. Marchioro, S. Moon, R. Humphry-Baker, J. Yum, J. E. Moser, M. Graetzel and N.-G. Park. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Sci. Rep.*, **2012**, 2, 591.
- [31] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science*, **2012**, 338, 643-647.
- [32] J. M. Ball, M. M. Lee, A. Hey and H. J. Snaith. Low-temperature processed meso-superstructured to thin-film perovskite solar cells. *Energy Environ. Sci.*, **2013**, 6, 1739-1743.
- [33] G. E. Eperon, V. M. Burlakov, P. Docampo, A. Goriely and H. J. Snaith. Morphological control for high performance, solution-processed planar heterojunction perovskite solar cells. *Adv. Funct. Mater.*, **2013**, 24, 151-157.
- [34] M. Liu, M. B. Johnston and H. J. Snaith. Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature*, **2013**, 501, 395-398.
- [35] O. Malinkiewicz, A. Yella, Y. H. Lee, G. M. Espallargas, M. Graetzel, M. K. Nazeeruddin and H. J. Bolink. Perovskite solar cells employing organic charge-transport layers. *Nat. Photonics*, **2014**, 8, 128-132.

-
- [36] J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C. Lim, J. A. Chang, Y. H. Lee, H. Kim, A. Sarkar and M. K. Nazeeruddin. Efficient inorganic-organic hybrid heterojunction solar cells containing perovskite compound and polymeric hole conductors. *Nat. Photonics*, **2013**, 7, 486-491.
- [37] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok. Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. *Nano Lett.*, **2013**, 13, 1764-1769.
- [38] J. Burschka, N. Pellet, S. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Graetzel. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature*, **2013**, 499, 316.
- [39] H. Zhou, Q. Chen, G. Li, S. Luo, T. B. Song, H. S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang. Interface engineering of highly efficient perovskite solar cells. *Science*, **2014**, 345, 542-546.
- [40] M. Graetzel. The light and shade of perovskite solar cells. *Nat. Mater.*, **2014**, 13, 838-842.
- [41] T. M. Koh, K. Fu, Y. Fang, S. Chen, T. Sum, N. Mathews, S. G. Mhaisalkar, P. P. Boix and T. Baikie. Formamidinium-containing metal-halide: an alternative material for near-IR absorption perovskite solar cells. *J. Phys. Chem. C.*, **2013**, 118, 16458-16462.
- [42] A. Amat, E. Mosconi, E. Ronca, C. Quarti, P. Umari, M. K. Nazeeruddin and M. Graetzel and F. De Angelis. Cation-induced band-gap tuning in organohalide perovskites: interplay of spin-orbit coupling and octahedra tilting. *Nano Lett.*, **2014**, 14, 3608-3616.
- [43] N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok.

- Compositional engineering of perovskite materials for high-performance solar cells. *Nature*, **2015**, 517, 476-480.
- [44] J. P. C. Baena, L. Steier, W. Tress, M. Saliba, S. Neutzner, T. Matsui, F. Giordano, T. J. Jacobsson, A. R. S. Kandada, S. M. Zakeeruddin, A. Petrozza, A. Abate, M. K. Nazeeruddin, M. Gratzel and A. Hagfeldt. Highly efficient planar perovskite solar cells through band alignment engineering. *Energy Environ. Sci.*, **2015**, 8, 2928-2934.
- [45] D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J. P. Correa Baena, J. D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Gratzel and A. Hagfeldt. Efficient luminescent solar cells based on tailored mixed-cation perovskites. *Sci. Adv.*, **2016**, 2, e1501170.
- [46] D. P. McMeekin, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Horantner, A. Haghighirad, N. Sakai, L. Korte, B. Rech, M. B. Johnston, L. M. Herz and H. J. Snaith. A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. *Science*, **2016**, 351, 151-155.
- [47] M. Saliba, T. Matsui, J. Seo, K. Domanski, J. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate and A. Hagfeldt. Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy Environ. Sci.*, **2016**, 9, 1989-1997.
- [48] M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt, M. Graetzel. Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. *Science*, **2016**, 354, 206-209.
- [49] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu and S. I. Seok. Solvent

- engineering for high-performance inorganic-organic hybrid perovskite solar cells. *Nature Mater.*, **2014**, 13, 897-903.
- [50] W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*, **2015**, 348, 1234-1237.
- [51] S. S. Shin, E. J. Yeom, W. S. Yang, S. Hur, M. G. Kim, J. Im, J. Seo, J. H. Noh and S. I. Seok. Colloidally prepared La-doped BaSnO₃ electrodes for efficient, photostable perovskite solar cells. *Science*, **2017**, 356, 167-171.
- [52] W. S. Yang, B.-W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, S. S. Shin, J. Seo, E. K. Kim, J. H. Noh, S. I. Seok. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. *Science*, **2017**, 356, 1376-1379.
- [53] M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop. Solar cell efficiency tables (version 50). *Prog. Photovolt.*, **2017**, 25, 668-676.
- [54] W. Shockley and H. J. Queisser. Detailed balance limit of efficiency of p-n junction solar cells. *J. Appl. Phys.*, **1961**, 32, 510-519.
- [55] L. Zuo, C.-C. Chueh, Y.-X. Xu, K.-S. Chen, Y. Zang, C.-Z. Li, H. Chen and A. K. Y. Jen. Microcavity-enhanced light-trapping for highly efficient organic parallel tandem solar cells. *Adv. Mater.*, **2014**, 26, 6778-6784.
- [56] A. R. B. M. Yusoff, D. Kim, H. P. Kim, F. K. Shneider, W. J. da Silva and J. Jang. A high efficiency solution processed polymer inverted triple-junction solar cell exhibiting a power conversion efficiency of 11.83%. *Energy Environ. Sci.*, **2015**, 8, 303-316.

- [57] P. Mailoa, C. D. Bailie, E. C. Johlin, E. T. Hoke, A. J. Akey, W. H. Nguyen, M. D. McGehee and T. Buonassisi. A 2-terminal perovskite/silicon multijunction solar cell enabled by a silicon tunnel junction. *Appl. Phys. Lett.*, **2015**, 106, 121105.
- [58] F. Meillaud, A. Shah, C. Droz, E. Vallat-Sauvain, C. Miazza. Efficiency limits for single-junction and tandem solar cells. *Sol. Energy Mater. Sol. Cells*, **2006**, 90, 2952-2959.
- [59] G. E. Eperon, T. Leijtens, K. A. Bush, T. Green, J. T.-W. Wang, D. P. McMeekin, G. Volonakis, R. L. Milot, D. J. Slotcavage, R. Beslile, J. B. Patel, E. S. Parrott, R. J. Sutton, W. Ma, F. Moghadam, B. Conings, A. Babayigit, H.-G. Boyen, F. Giustino, L. M. Herz, M. B. Johnston, M. D. McGehee and H. J. Snaith. Perovskite-perovskite tandem photovoltaics with optimized band gaps. *Science*, **2016**, 354, 861-865.
- [60] B. Chen, Y. Bai, Z. Yu, T. Li, X. Zheng, Q. Dong, L. Shen, M. Boccard, A. Gruverman and Z. Holman. Efficient Semitransparent Perovskite Solar Cells for 23.0%-Efficiency Perovskite/Silicon Four-Terminal Tandem Cells. *Adv. Energy Mater.*, **2016**, 6, 1601128.
- [61] S. Albrecht, M. Saliba, J. P. C. Baena, F. Lang, L. Kegelmann, M. Mews, L. Steier, A. Abate, J. Rappich and L. Korte. Monolithic perovskite/silicon-heterojunction tandem solar cells processed at low temperature. *Energy Environ. Sci.*, **2016**, 9, 81-88.
- [62] K. A. Bush, A. Palmstrom, Z. J. Yu, M. Boccard, R. Cheacharoen, J. P. Mailoa, D. P. McMeekin, R. L. Z. Hoyer, C. D. Bailie, T. Leijtens. 23.6%-efficient monolithic perovskite/silicon tandem solar cells with improved stability. *Nat. Energy*, **2017**, 2, 17009. DOI: 10.1038/nenergy.2017.9

- [63] M. Anaya, J. P. Correa-Baena, G. Lozano, M. Saliba, P. Anguita, B. Roose, A. Abate, U. Steiner, M. Graetzel and M. E. Calvo. Optical analysis of $\text{CH}_3\text{NH}_3\text{Sn}_x\text{Pb}_{1-x}\text{I}_3$ absorbers: a roadmap for perovskite-on-perovskite tandem solar cells. *J. Mater. Chem. A*, **2016**, 4, 11214-11221.
- [64] B. E. Lassiter, C. Kyle Renshaw, S. R. Forrest. Understanding tandem organic photovoltaic cell performance. *J. Appl. Phys.*, **2013**, 113, 214505.
- [65] T. Todorov, O. Gunawan and S. Guha. A road towards 25% efficiency and beyond: perovskite tandem solar cells. *Mol. Syst. Des. Eng.*, **2016**, 1, 370-376.
- [66] S. Yang, W. Fu, Z. Zhang, H. Chen, C.-Z. Li. Recent advances in perovskite solar cells: efficiency, stability and lead-free perovskite. *J. Mater. Chem. A*, **2017**. DOI: 10.1039/C7TA00366H
- [67] Z. Gu, L. Zuo, T. T. Larsen-Olsen, T. Ye, G. Wu, F. C. Krebs and H. Chen. Interfacial engineering of self-assembled monolayer modified semi-roll-to-roll planar heterojunction perovskite solar cells on flexible substrates. *J. Mater. Chem. A*, **2015**, 3, 24254-24260.
- [68] T. M. Schmidt, T. T. Larsen-Olsen, J. E. Carle, D. Angmo and F. C. Krebs. Up-scaling of perovskite solar cells: fully ambient roll processing of flexible perovskite solar cells with printed back electrodes. *Adv. Energy Mater.*, **2015**, 5, 1500569.
- [69] B. Conings, A. Babayigit, M. T. Klug, S. Bai, N. Gauquelin, N. Sakai, J. T.-W. Wang, J. Verbeeck, H.-G. Boyen and H. J. Snaith. A Universal Deposition Protocol for Planar Heterojunction Solar Cells with High Efficiency Based on Hybrid Lead Halide Perovskite Families. *Adv. Mater.*, **2016**, 28, 10701-10709.
- [70] F. Ye, H. Chen, F. Xie, W. Tang, M. Yin, J. He, E. Bi, Y. Wang, X. Yang and L. Han. Soft-cover deposition of scaling-up uniform perovskite thin films for high cost-performance solar cells. *Energy Environ. Sci.*, **2016**, 9, 2295-2301.

- [71] B. Conings, J. Drijkoningen, N. Gauquelin, A. Babayigit, J. D'Haen, L. D'Olieslaeger, A. Ethirajan, J. Verbeeck, J. Manca and E. Mosconi. Intrinsic thermal instability of methylammonium lead trihalide perovskite. *Adv. Energy Mater.*, **2015**, 5, 1500477.
- [72] R. J. Sutton, G. E. Eperon, L. Miranda, E. S. Parrott, B. A. Kamino, J. B. Patel, M. T. Hoerantner, M. B. Johnston, A. A. Haghighirad and D. T. Moore, *Adv. Energy Mater.*, **2016**, 6, 1502458.
- [73] Q. A. Akkerman, V. D'Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato and L. Manna. Tuning the optical properties of cesium lead halide perovskite nanocrystals by anion exchange reactions. *J. Am. Chem. Soc.*, **2015**, 137, 10276-10281.
- [74] C. D. Bailie and M. D. McGehee. High-efficiency tandem perovskite solar cells. *MRS Bull*, **2015**, 40, 681-686.
- [75] M. Kulbak, D. Cahen and G. Hodes. How important is the organic part of lead halide perovskite photovoltaic cells? Efficient CsPbBr₃ cells. *J. Phys. Chem. Lett.*, **2015**, 6, 2452-2456.
- [76] R. E. Beal, D. J. Slotcavage, T. Leijtens, A. R. Bowring, R. A. Belisle, W. H. Nguyen, G. F. Burkhard, E. T. Hoke and M. D. McGehee. Cesium lead halide perovskites with improved stability for tandem solar cells. *J. Phys. Chem. Lett.*, **2016**, 7, 746-751.
- [77] H. Choi, J. Jeong, H. Kim, S. Kim, B. Walker, G. Kim and J. Y. Kim. Cesium-doped methylammonium lead iodide perovskite light absorber for hybrid solar cells. *Nano Energy*, **2014**, 7, 80-85.
- [78] C. Yi, J. Luo, S. Meloni, A. Boziki, N. Ashari-Astani, C. Graetzel, S. M. Za-keeruddin, U. Roethlisberger and M. Graetzel. Entropic stabilization of mixed

- A-cation ABX_3 metal halide perovskites for high performance perovskite solar cells. *Energy Environ. Sci.*, **2016**, 9, 656-662.
- [79] J.-W. Lee, D.-H. Kim, H.-S. Kim, S.-W. Seo, S. M. Cho and N.-G. Park. Formamidinium and cesium hybridization for photo-and moisture-stable perovskite solar cell. *Adv. Energy Mater.*, **2015**, 5, 1501310.
- [80] A. Binek, F. C. Hanusch, P. Docampo and T. Bein. Stabilization of the trigonal high-temperature phase of formamidinium lead iodide. *J. Phys. Chem. Lett.*, **2015**, 6, 1249-1253.
- [81] Z. Li, M. Yang, J. Park, S. Wei, J. J. Berry, K. Zhu. Stabilizing perovskite structures by tuning tolerance factor: formation of formamidinium and cesium lead iodide solid-state alloys. *Chem. Mater.*, **2015**, 28, 284-292.
- [82] J. Song, X. F. Wang, G. Chen, W. Tian and T. Miyasaka. Highly efficient and stable low-temperature processed ZnO solar cells with triple cation perovskite absorber. *J. Mater. Chem. A.*, **2017**, 5, 13439-13447.
- [83] A. J. Pearson, G. E. Eperon, P. E. Hopkinson, S. N. Habisreutinger, J. T. W. Wang, H. J. Snaith and N. C. Greenham. Oxygen Degradation in Mesoporous $\text{Al}_2\text{O}_3/\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Perovskite Solar Cells: Kinetics and Mechanisms. *Adv. Energy Mater.*, **2016**, 6, 1600014.
- [84] T. Leijtens, K. A. Bush, R. Cheacharoen, R. Beal, A. R. Bowring and M. D. McGehee. Towards enabling stable lead halide perovskite solar cells; interplay between structural, environmental, and thermal stability. *J. Mater. Chem. A*, **2017**, 5, 11483-11500.
- [85] N. Aristidou, I. Sanchez-Molina, T. Chotchuangchutchaval, M. Brown, L. Martinez, T. Rath and S. A. Haque. The role of oxygen in the degradation of methyl-

- ammonium lead trihalide perovskite photoactive layers. *Angew. Chem., Int. Ed.*, **2015**, 54, 8208-8212.
- [86] Z. Wang, D. P. McMeekin, N. Sakai, S. van Reenen, K. Wojciechowski, J. B. Patel, M. B. Johnston and H. J. Snaith. Efficient and Air-Stable Mixed-Cation Lead Mixed-Halide Perovskite Solar Cells with n-Doped Organic Electron Extraction Layers. *Adv. Mater.*, **2017**, 29, 1604186.
- [87] J. A. Christians, P. A. Miranda Herrera and P. V. Kamat. Transformation of the Excited State and Photovoltaic Efficiency of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite upon Controlled Exposure to Humidified Air. *J. Am. Chem. Soc.*, **2015**, 137, 1530-1538.
- [88] S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas and H. J. Snaith. Carbon nanotube/polymer composites as a highly stable hole collection layer in perovskite solar cells. *Nano Lett.*, **2014**, 14, 5561-5568.
- [89] A. Leguy, Y. Hu, M. Campoy-Quiles, M. I. Alonso, O. J. Weber, P. Azarhoosh, M. van Schilfgaarde, M. T. Weller, T. Bein and J. Nelson. Reversible hydration of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in films, single crystals, and solar cells. *Chem. Mater.*, **2015**, 27, 3397-3407.
- [90] O. Knop, R. E. Wasylshen, M. A. White, T. S. Cameron and M. J. M. Van Oort. Alkylammonium lead halides. Part 2. $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) perovskites: cuboctahedral halide cages with isotropic cation reorientation. *Can. J. Chem.*, **1990**, 68, 412-422.
- [91] T. Leijtens, G. E. Eperon, N. K. Noel, S. N. Habisreutinger, A. Petrozza and H. J. Snaith. Stability of Metal Halide Perovskites. *Adv. Energy Mater.*, **2015**, 5, 1500963.

- [92] Y. Sun, J. Peng, Y. Chen, Y. Yao and Z. Liang. Triple-cation mixed-halide perovskites: towards efficient, annealing-free and air-stable solar cells enabled by $\text{Pb}(\text{SCN})_2$ additive. *Sci. Rep.*, **2017**, 7, 46193.
- [93] E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa and M. D. McGehee. Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. *Chem. Sci.*, **2015**, 6, 613-617.
- [94] A. J. Barker, A. Sadhanala, F. Deschler, M. Gandini, S. P. Senanayak, P. M. Pearce, E. Mosconi, A. Pearson, Y. Wu, A. R. Srimath Kandada, T. Leijtens, F. De Angelis, S. E. Dutton, A. Petrozza and R. H. Friend. Defect-Assisted Photoinduced Halide Segregation in Mixed-Halide Perovskite Thin Films. *ACS Energy Lett.*, **2017**, 2, 1416-1424.
- [95] C. G. Bischak, C. L. Hetherington, H. Wu, S. Aloni, D. F. Ogletree, D. T. Limmer, and N. S. Ginsberg. Origin of reversible photoinduced phase separation in hybrid perovskites. *Nano Lett.*, **2017**, 1028-1033.
- [96] M. Hu, C. Bi, Y. Yuan, Y. Bai and J. Huang. Stabilized Wide Bandgap $\text{MAPbBr}_x\text{I}_{3-x}$ Perovskite by Enhanced Grain Size and Improved Crystallinity. *Adv. Sci.*, **2015**, 3, 1500301.
- [97] E. L. Unger, L. Kegelmann, K. Suchan, D. Soerell, L. Korte and S. Albrecht. Roadmap and roadblocks for the band gap tunability of metal halide perovskites. *J. Mater. Chem. A*, **2017**, 5, 11401-11409.
- [98] A. Kovalsky, L. Wang, G. T. Marek, C. Burda, and J. S. Dyck. Thermal Conductivity of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and CsPbI_3 : Measuring the Effect of the Methylammonium Ion on Phonon Scattering. *J. Phys. Chem. C*, **2017**, 3228-3233.
- [99] D. J. Slotcavage, H. I. Karunadasa and M. D. McGehee, Light-Induced Phase

- Segregation in Halide-Perovskite Absorbers. *ACS Energy Lett.*, **2016**, 1, 1199-1205.
- [100] X. Yang, X. Yan, W. Wang, X. Zhu, H. Li, W. Ma, and C. Sheng. Light induced metastable modification of optical properties in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ perovskite films: Two-step mechanism. *Org. Electr.*, **2016**, 34, 79-83.
- [101] P. Fedeli, F. Gazza, D. Calestani, P. Ferro, T. Besagni, A. Zappettini, G. Calestani, E. Marchi, P. Ceroni, and R. Mosca. Influence of the Synthetic Procedures on the Structural and Optical Properties of Mixed-Halide (Br, I) Perovskite Films. *J. Phys. Chem. C*, **2015**, 119, 21304-21313.
- [102] L. M. Herz. Charge-Carrier Mobilities in Metal Halide Perovskites: Fundamental Mechanisms and Limits. *ACS Energy Lett.*, **2017**, 2, 1539-1548.
- [103] J. S. Manser, J. A. Christians and P. V. Kamat. Intriguing optoelectronic properties of metal halide perovskites. *Chem. Rev.*, **2016**, 116, 12956-13008.
- [104] C. Wehrenfennig, M. Liu, H. J. Snaith, M. B. Johnston and L. M. Herz. Charge-carrier dynamics in vapour-deposited films of the organolead halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. *Energy Environ. Sci.*, **2014**, 7, 2269-2275.
- [105] C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith and L. M. Herz. High charge carrier mobilities and lifetimes in organolead trihalide perovskites. *Adv. Mater.*, **2014**, 26, 1584.
- [106] D. W. deQuilettes, S. M. Vorpahl, S. D. Stranks, H. Nagaoka, G. E. Eperon, M. E. Ziffer, H. J. Snaith and D. S. Ginger. Impact of microstructure on local carrier lifetime in perovskite solar cells. *Science*, **2015**, 348, 683-686.
- [107] W. Yin, T. Shi and Y. Yan. Unique properties of halide perovskites as possible origins of the superior solar cell performance. *Adv. Mater.*, **2014**, 26, 4653-4658.

- [108] E. Edri, S. Kirmayer, A. Henning, S. Mukhopadhyay, K. Gartsman, Y. Rosenwaks, G. Hodes and D. Cahen. Why lead methylammonium tri-iodide perovskite-based solar cells require a mesoporous electron transporting scaffold (but not necessarily a hole conductor). *Nano Lett.*, **2014**, 14, 1000-1004.
- [109] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith. Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science*, **2013**, 342, 341-344.
- [110] T. Du, N. Wang, H. Chen, H. Lin and H. He. Comparative study of vapor-and solution-crystallized perovskite for planar heterojunction solar cells. *ACS Appl. Mater. Interfaces.*, **2015**, 7, 3382-3388.
- [111] E. Mosconi, A. Amat, M. K. Nazeeruddin, M. Graetzel and F. De Angelis. First-Principles Modeling of Mixed Halide Organometal Perovskites for Photovoltaic Applications. *J. Phys. Chem. C*, **2013**, 117, 13902-13913.
- [112] J. Even, L. Pedesseau, C. Katan, M. Kepenekian, J. S. Laurent, D. Saponi and E. Deleporte. Solid-state physics perspective on hybrid perovskite semiconductors. *J. Phys. Chem. C*, **2015**, 119, 10161-10177.
- [113] I. B. Koutselas, L. Ducasse and G. C. Papavassiliou. Electronic properties of three- and low-dimensional semiconducting materials with Pb halide and Sn halide units. *J. Phys.: Condens. Matter*, **1996**, 8, 1217-1227.
- [114] T. Umebayashi, K. Asai, T. Kondo and A. Nakao. Electronic structures of lead iodide based low-dimensional crystals. *Phys. Rev. B*, **2003**, 67, 155405.
- [115] C. Motta, F. El-Mellouhi, S. Kais, N. Tabet, F. Alharbi and S. Sanvito. Revealing the role of organic cations in hybrid halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Nat. Commun.*, **2015**, 6, 7026.

- [116] A. Filippetti and A. Mattoni. Hybrid perovskites for photovoltaics: Insights from first principles. *Phys. Rev. B*, **2014**, 89, 125203.
- [117] L. K. Ono, E. J. Juarez-Perez and Y. Qi. Progress on Novel Perovskite Materials and Solar Cells with Mixed Cations and Halide Anions. *ACS Appl. Mater. Interfaces*, **2017**.
- [118] T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes and D. Cahen. Hybrid organic-inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties. *Nat. Rev. Mater.*, **2016**, 1, 15007.
- [119] M. Hirasawa, T. Ishihara, T. Goto and K. Uchida. Magnetoabsorption of the lowest exciton in perovskite-type compound $(\text{CH}_3\text{NH}_3)\text{PbI}_3$. *Phys. B*, **1994**, 201, 427-430.
- [120] Y. Yamada, T. Nakamura, M. Endo, A. Wakamiya and Y. Kanemitsu. Photo-carrier recombination dynamics in perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ for solar cell applications. *J. Am. Chem. Soc.*, **2014**, 136, 11610-11613
- [121] S. Sun, T. Salim, N. Mathews, M. Duchamp, C. Boothroyd, G. Xing, T. C. Sum and Y. M. Lam. The origin of high efficiency in low-temperature solution-processable bilayer organometal halide hybrid solar cells. *Energy Environ. Sci.*, **2014**, 7, 399-407.
- [122] V. D’Innocenzo, G. Grancini, M. J. Alcocer, A. R. S. Kandada, S. D. Stranks, M. M. Lee, G. Lanzani, H. J. Snaith and A. Petrozza. Excitons versus free charges in organo-lead tri-halide perovskites. *Nat. Commun.*, **2014**, 5, 3586.
- [123] A. Miyata, A. Mitiglu, P. Plochocka, O. Portugall O, J. T. W. Wang, S. D. Stranks, H. J. Snaith and R. J. Nicholas. Direct measurement of the exciton binding energy and effective masses for charge carriers in an organic-inorganic tri-halide perovskite. *Nat. Phys.*, **2015**, 11, 582-587.

- [124] S. De Wolf, J. Holovsky, S. Moon, P. Loeper, B. Niesen, M. Ledinsky, F. Haug, J. Yum and C. Ballif. Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. *J. Phys. Chem. Lett.*, **2014**, 5, 1035-1039.
- [125] A. Sadhanala, F. Deschler, T. H. Thomas, S. E. Dutton, K. C. Goedel, F. C. Hanusch, M. L. Lai, U. Steiner, T. Bein and P. Docampo. Preparation of single-phase films of $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ with sharp optical band edges. *J. Phys. Chem. Lett.*, **2014**, 5, 2501-2505.
- [126] F. Brivio, K. T. Butler, A. Walsh and M. van Schilfgaarde. Relativistic quasi-particle self-consistent electronic structure of hybrid halide perovskite photovoltaic absorbers. *Phys. Rev. B*, **2014**, 89, 155204.
- [127] T. M. Brenner, D. A. Egger, A. M. Rappe, L. Kronik, G. Hodes, David Cahen. Are mobilities in hybrid organic-inorganic halide perovskites actually ‘high’? *J. Phys. Chem. Lett.*, **2015** 6, 4754-4757.
- [128] S. M. Sze and K. K. Ng. Physics of Semiconductor Devices, *John Wiley*, **2006**.
- [129] C. Ponseca Jr and V. Sundstroem. Revealing the ultrafast charge carrier dynamics in organo metal halide perovskite solar cell materials using time resolved THz spectroscopy. *Nanoscale*, **2016**, 8, 6249-6257.
- [130] R. T. Williams and K. S. Song. The self-trapped exciton. *J. Phys. Chem. Solids*, **1990**, 51, 679-716.
- [131] M. B. Johnston and L. M. Herz. Hybrid Perovskites for Photovoltaics: Charge-Carrier Recombination, Diffusion, and Radiative Efficiencies. *Acc. Chem. Res.*, **2016**, 49, 146-154.

- [132] C. Wehrenfennig, M. Liu, H. J. Snaith, M. B. Johnston and L. M. Herz. Homogeneous Emission Line Broadening in the Organo Lead Halide Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$. *J. Phys. Chem. Lett.*, **2014**, 5, 1300-1306.
- [133] R. L. Milot, G. E. Eperon, H. J. Snaith, M. B. Johnston and L. M. Herz. Temperature-dependent charge-carrier dynamics in $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Adv. Funct. Mater.*, **2015**, 25, 6218-6227.
- [134] T. J. Savenije, C. S. Ponseca, L. Kunneman, M. Abdellah, K. Zheng, Y. Tian, Q. Zhu, S. E. Canton, I. G. Scheblykin, T. Pullerits, A. Yartsev and V. Sundstroem. Thermally activated exciton dissociation and recombination control the carrier dynamics in organometal halide perovskite. *J. Phys. Chem. Lett.*, **2014**, 5, 2189-2194.
- [135] D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent and O. M. Bakr. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science*, **2015**, 347, 519-522.
- [136] Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao and J. Huang. Electron-hole diffusion lengths $>175\ \mu\text{m}$ in solution-grown $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals. *Science*, **2015**, 347, 967-970.
- [137] C. G. Bischak, E. M. Sanehira, J. T. Precht, J. M. Luther and N. S. Ginsberg. Heterogeneous Charge Carrier Dynamics in Organic-Inorganic Hybrid Materials: Nanoscale Lateral and Depth-Dependent Variation of Recombination Rates in Methylammonium Lead Halide Perovskite Thin Films. *Nano Lett.*, **2015**, 15, 4799-4807.
- [138] I. Visoly-Fisher, S. R. Cohen, K. Gartsman, A. Ruzin and D. Cahen. Under-

- standing the Beneficial Role of Grain Boundaries in Polycrystalline Solar Cells from Single-Grain-Boundary Scanning Probe Microscopy. *Adv. Funct. Mater.*, **2006**, 16, 649-660.
- [139] T. Distefano and J. Cuomo. Reduction of grain boundary recombination in polycrystalline silicon solar cells. *Appl. Phys. Lett.*, **1977**, 30, 351-353.
- [140] C. Li, Y. L. Wu, J. Poplawsky, T. J. Pennycook, N. Paudel, W. J. Yin, S. J. Haigh, M. P. Oxley, A. R. Lupini, M. Al-Jassim, S. J. Pennycook and Y. F. Yan. Grain-boundary-enhanced carrier collection in CdTe solar cells. *Phys. Rev. Lett.*, **2014**, 112, 156103.
- [141] M. Gloeckler, J. R. Sites, W. K. Metzger. Grain-boundary recombination in Cu (In, Ga) Se₂ solar cells. *J. Appl. Phys.*, **2005**, 98, 113704.
- [142] W. J. Yin, T. Shi, Y. Yan. Unusual defect physics in CH₃NH₃PbI₃ perovskite solar cell absorber. *Appl. Phys. Lett.*, **2014**, 104, 063903.
- [143] A. Walsh, D. O. Scanlon, S. Chen, X. Gong, S.-H. Wei. Self-Regulation Mechanism for Charged Point Defects in Hybrid Halide Perovskites. *Angew. Chem.*, **2015**, 127, 1811-1814.
- [144] R. Menzel. Photonics: Linear and nonlinear interactions of laser light and matter. *Springer*, **2013**.
- [145] H. Kuzmany. Solid-State Spectroscopy. *Springer*, **2009**.
- [146] R. Miles. Terahertz Frequency Detection and Identification of Materials and Objects. *Springer Netherlands*, **2007**.
- [147] D. G. Cooke, F. C. Krebs and P. U. Jepsen. Direct Observation of Sub-100 fs Mobile Charge Generation in a Polymer-Fullerene Film. *Phys. Rev. Lett.*, **2012**, 079901.

-
- [148] X. C. Zhang, B. B. Hu, J. T. Darrow and D. H. Auston. Generation of femto-second electromagnetic pulses from semiconductor surfaces. *Appl. Phys. Lett.*, **1990**, 1011-1013.
- [149] X.C. Zhang. Introduction to THz Wave Photonics, *Springer US*, **2010**.
- [150] B. B. Hu, X. C. Zhang, D. H. Auston and P. R. Smith. Generation of femto-second electromagnetic pulses from semiconductor surfaces. *Appl. Phys. Lett.*, **1990**, 56, 506-508.
- [151] A. Rice, Y. Jin, X. F. Ma, X.-C. Zhang, D. Bliss, J. Larkin and M. Alexander. Terahertz optical rectification from $\langle 110 \rangle$ zinc-blende crystals. *Appl. Phys. Lett.*, **1994**, 64, 1324-1326.
- [152] K. H. Yang, P. L. Richards and Y. R. Shen. Generation of far-infrared radiation by picosecond light pulses in LiNbO_3 . *Appl. Phys. Lett.*, **1971**, 19, 320-323.
- [153] C. A. Schmuttenmaer. Exploring dynamics in the far-infrared with terahertz spectroscopy. *Chem. Rev.*, **2004**, 104, 1759-1779.
- [154] M. Bass, P. A. Franken, J. F. Ward and G. Weinreich. Optical rectification. *Phys. Rev. Lett.*, **1962**, 9, 446.
- [155] P. U. Jepsen, D. G. Cooke and M. Koch. Terahertz spectroscopy and imaging- Modern techniques and applications. *Laser Photon. Rev.*, **2011**, 5, 124-166.
- [156] P. Tiwana. Ultrafast charge dynamics in mesoporous materials used in dye-sensitized solar cells, PhD thesis, University of Oxford. **2013**.
- [157] Q. Wu and X. C. Zhang. Free-space electro-optic sampling of terahertz beams. *Appl. Phys. Lett.*, **1995**, 67, 3525.

- [158] M. Tani, K. Sakai and H. Mimura. Ultrafast photoconductive detectors based on semi-insulating GaAs and InP. *Jpn. J. Appl. Phys. Part 2 - Lett.*, **1997**, 36, 1175-1178.
- [159] J. Dai, X. Xie and X. C. Zhang. Coherent control of THz wave generation in ambient air. *Phys. Rev. Lett.*, **2006**, 97, 103903.
- [160] A. Nahata, A. S. Weling and T. F. Heinz. A wideband coherent terahertz spectroscopy system using optical rectification and electro-optic sampling. *Appl. Phys. Lett.*, **1996**, 69, 2321.
- [161] X. Yin. Terahertz Imaging for Biomedical Application. Pattern Recognition and Tomographic Reconstruction. *Springer US*, **2012**.
- [162] F.C.A Pockels. Lehrbuch der Kristallogoptik. *BG Teubner*, **1906**, 19.
- [163] M. C. Beard, G. M. Turner and C. A. Schmuttenmaer. Terahertz spectroscopy. *J. Phys. Chem. B*, **2002**, 106, 7146-7159.
- [164] C. Winnewisser, P. U. Jepsen, M. Schall, V. Schyja and H. Helm. Electro-optic detection of THz radiation in LiTaO₃, LiNbO₃ and ZnTe. *Appl. Phys. Lett.*, **1997**, 70, 3069-3071.
- [165] H.-K. Nienhuys and V. Sundstroem. Intrinsic complications in the analysis of optical-pump, terahertz probe experiments. *Phys. Rev. B*, **2005**, 71, 235110.
- [166] G.D. Gilliland. Photoluminescence spectroscopy of crystalline semiconductors. *Materials Science and Engineering: R: Reports*, **1997**, 18, 99-399.
- [167] R. C. Hilborn. Einstein coefficients, cross sections, f values, dipole moments, and all that. *American J. Phys.*, **1982**, 50, 982-986.
- [168] D. V. O'Connor, D. Phillips. Time-correlated Single Photon Counting. *Academic Press*, **1984**.

- [169] W. Becker. Advanced Time-Correlated Single Photon Counting Techniques. *Springer*, **2005**.
- [170] S. D. Stranks. Investigating Carbon Nanotube Polymer Blends for Organic Solar Cell Applications. PhD thesis, University of Oxford, **2011**.
- [171] G. Nofuentes, C. A. Gueymard, J. Aguilera, M. D. Perez-Godoy and F. Charte. Is the average photon energy a unique characteristic of the spectral distribution of global irradiance? *Solar Energy*, **2017**, 149, 32-43.
- [172] C. A. Gueymard. Daily spectral effects on concentrating PV solar cells as affected by realistic aerosol optical depth and other atmospheric conditions. *Proc. SPIE*, **2009**, 7410, 741007.
- [173] F. Hao, C. C. Stoumpos, D. H. Cao, R. P. Chang and M. G. Kanatzidis, *Nat. Photonics*, **2014**, 8, 489.
- [174] N. K. Noel, S. D. Stranks, A. Abate, C. Wehrenfennig, S. Guarnera, A. Haghighirad, A. Sadhanala, G. E. Eperon, S. K. Pathak, M. B. Johnston, A. Petrozza, L. M. Herz and H. J. Snaith. Lead-free organic-inorganic tin halide perovskites for photovoltaic applications. *Energy Environ. Sci.*, **2014**, 7, 3061-3068.
- [175] R. S. Sanchez, V. Gonzalez-Pedro, J. Lee, N. Park, Y. S. Kang, I. Mora-Sero and J. Bisquert. Slow dynamic processes in lead halide perovskite solar cells. Characteristic times and hysteresis. *J. Phys. Chem. Lett.*, **2014**, 5, 2357-2363.
- [176] J. Im, I. Jang, N. Pellet, M. Graetzel and N. Park. Growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$ cuboids with controlled size for high-efficiency perovskite solar cells. *Nat. Nanotechnol.*, **2014**, 9, 927-932.

- [177] S. A. Kulkarni, T. Baikie, P. P. Boix, N. Yantara, N. Mathews and S. Mhaisalkar. Band-gap tuning of lead halide perovskites using a sequential deposition process. *J. Mater. Chem. A*, **2014**, 2, 9221-9225.
- [178] P. Gao, M. Graetzel and M. K. Nazeeruddin. Organohalide lead perovskites for photovoltaic applications. *Energy Environ. Sci.*, **2014**, 7, 2448-2463.
- [179] A. Walsh. Principles of chemical bonding and band gap engineering in hybrid organic-inorganic halide perovskites. *J. Phys. Chem. C*, **2015**, 119, 5755-5760.
- [180] H. Nienhuys and V. Sundstroem. Intrinsic complications in the analysis of optical-pump, terahertz probe experiments. *Phys. Rev. B*, **2005**, 71, 235110.
- [181] A. Haug. Auger recombination in direct-gap semiconductors: band-structure effects. *J. Phys. C: Solid State Phys.*, **1983**, 16, 4159.
- [182] P. Liang, C. Chueh, X. Xin, F. Zuo, S. T. Williams, C. Liao and A. K. Jen. High Performance Planar-Heterojunction Solar Cells Based on Ternary Halide Large-Band-Gap Perovskites. *Adv. Energy Mater.*, **2015**, 5, 1400960.
- [183] N. Kedem, T. M. Brenner, M. Kulbak, N. Schaefer, S. Levchenko, I. Levine, D. Abou-Ras, G. Hodes and D. Cahen. Light-induced increase of electron diffusion length in a p-n junction type $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite solar cell. *J. Phys. Chem. Lett.*, **2015**, 6, 2469-2476.
- [184] J. Pan, C. Mu, Q. Li, W. Li, D. Ma and D. Xu. Room-Temperature, Hydrochloride-Assisted, One-Step Deposition for Highly Efficient and Air-Stable Perovskite Solar Cells. *Adv. Mater.*, **2016**, 28, 8309-8314.
- [185] G. E. Eperon, G. M. Paterno, R. J. Sutton, A. Zampetti, A. A. Haghighirad, F. Cacialli and H. J. Snaith. Inorganic caesium lead iodide perovskite solar cells. *J. Mater. Chem. A*, **2015**, 3, 19688-19695.

- [186] Q. Wang, B. Chen, Y. Liu, Y. Deng, Y. Bai, Q. Dong and J. Huang. Scaling behavior of moisture-induced grain degradation in polycrystalline hybrid perovskite thin films. *Energy Environ. Sci.*, **2017**, 10, 516-522.
- [187] W. Tress, N. Marinova, O. Inganaes, M. K. Nazeeruddin, S. M. Zakeeruddin and M. Graetzel. Predicting the open-circuit voltage of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells using electroluminescence and photovoltaic quantum efficiency spectra: the role of radiative and non-radiative recombination. *Adv. Energy Mater.*, **2014**, 5, 1400812.
- [188] K. Tvingstedt, O. Malinkiewicz, A. Baumann, C. Deibel, H. J. Snaith, V. Dyakonov and H. J. Bolink. Radiative efficiency of lead iodide based perovskite solar cells. *Sci. Rep.* 4, **2014**, 6071.
- [189] H. J. Snaith. Estimating the maximum attainable efficiency in dye-sensitized solar cells. *Adv. Funct. Mater.*, **2010**, 20, 13-19.
- [190] U. Rau. Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells. *Phys. Rev. B*, **2007**, 76, 085303.
- [191] Y. Zhou, M. Yang, O. S. Game, W. Wu, J. Kwun, M. A. Strauss, Y. Yan, J. Huang, K. Zhu and N. P. Padture. Manipulating crystallization of organolead mixed-halide thin films in antisolvent baths for wide-bandgap perovskite solar cells. *ACS Appl. Mater. Interfaces*, **2016**, 8, 2232-2237.
- [192] R. Lindblad, N. K. Jena, B. Philippe, J. Oscarsson, D. Bi, A. Lindblad, S. Mandal, B. Pal, D. D. Sarma, O. Karis, H. Siegbahn, E. M. J. Johansson, M. Odellius and H. M. Rensmo. Perovskites for photovoltaics: a combined review of organic-inorganic halide perovskites and ferroelectric oxide perovskites. *J. Phys. Chem. C*, **2015**, 119, 1818-1825.

- [193] T. J. Jacobsson, J. Correa-Baena, M. Pazoki, M. Saliba, K. Schenk, M. Graetzel and A. Hagfeldt. Exploration of the compositional space for mixed lead halogen perovskites for high efficiency solar cells. *Energy Environ. Sci.*, **2016**, 9, 1706-1724.
- [194] <http://abulafia.mt.ic.ac.uk/shannon/ptable.php>
(Accessed 8/7/2016).
- [195] J. T.-W. Wang, Z. Wang, S. Pathak, W. Zhang, D. W. DeQuilettes, F. Wisnivesky-Rocca-Rivarola, J. Huang, P. K. Nayak, J. B. Patel, H. A. Mohd Yusof, Y. Vaynzof, R. Zhu, I. Ramirez, J. Zhang, C. Ducati, C. Grovenor, M. B. Johnston, D. S. Ginger, R. J. Nicholas and H. J. Snaith. Efficient perovskite solar cells by metal ion doping. *Energy Environ. Sci.*, **2016**, 9, 2892-2901.
- [196] P. Scherrer. Kolloidchemie Ein Lehrbuch, *Springer*, 387-409, **1912**.
- [197] J. I. Langford and A. Wilson. Scherrer after sixty years: a survey and some new results in the determination of crystallite size. *J. Appl. Crystallogr.*, **1978**, 11, 102-113.
- [198] W. Nie, H. Tsai, R. Asadpour, J. C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H. L. Wang and A. D. Mohite. High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science*, **2015**, 347, 522-525.
- [199] J. Kim, S. Lee, J. H. Lee and K. Hong. The role of intrinsic defects in methylammonium lead iodide perovskite. *J. Phys. Chem. Lett.*, **2014**, 5, 1312-1317.
- [200] R. Long, J. Liu and O. V. Prezhdo. Unravelling the effects of grain boundary and chemical doping on electron-hole recombination in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite by time-domain atomistic simulation. *J. Am. Chem. Soc.*, **2016**, 138, 3884-3890.

- [201] F. Brivio, C. Caetano and A. Walsh. Band alignment of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ thin films by vacuum deposition. *J. Phys. Chem. Lett.*, **2016**, 7, 1083-1087.
- [202] A. D. Wright, C. Verdi, R. L. Milot, G. E. Eperon, M. A. Perez-Osorio, H. J. Snaith, F. Giustino, M. B. Johnston and L. M. Herz. Electron-phonon coupling in hybrid lead halide perovskites. *Nat. Commun.*, **2016**, 7, 11755.
- [203] Y. Shao, Y. Fang, T. Li, Q. Wang, Q. Dong, Y. Deng, Y. Yuan, H. Wei, M. Wang and A. Gruverman. Grain boundary dominated ion migration in polycrystalline organic-inorganic halide perovskite films. *Energy Environ. Sci.*, **2016**, 9, 1752-1759.
- [204] T. S. Sherkar, C. Momblona, L. Gil-Escrig, J. Avila, M. Sessolo, H. J. Bolink and L. J. A. Koster. Recombination in Perovskite Solar Cells: Significance of Grain Boundaries, Interface Traps, and Defect Ions. *ACS Energy Lett.*, **2017**, 2, 1214-1222.
- [205] G. F. Samu, C. Janaky and P. V. Kamat. A Victim of Halide Ion Segregation. How Light Soaking Affects Solar Cell Performance of Mixed Halide Lead Perovskites. *ACS Energy Lett.*, **2017**, 1860-1861.
- [206] W. Travis, E. Glover, H. Bronstein, D. Scanlon and R. Palgrave. On the application of the tolerance factor to inorganic and hybrid halide perovskites: a revised system. *Chem. Sci.*, **2016**, 7, 4548-4556.