

Direct Optical Characterization of Carrier Transport and Structural Properties in Halide Perovskite Materials

by

Wenhao Li

B. S., Lanzhou University, 2014

Sc. M., Brown University, 2017

A dissertation submitted in partial fulfillment of the
requirements for the Degree of Doctor of Philosophy
in the Department of Physics at Brown University

Providence, Rhode Island

October 2019

This dissertation by Wenhao Li is accepted in its present form by
the Department of Physics as satisfying the dissertation requirement
for the degree of Doctor of Philosophy.

Date _____

Rashid Zia, Director

Recommended to the Graduate Council

Date _____

Nitin Padture, Reader

Date _____

Robert Pelcovits, Reader

Approved by the Graduate Council

Date _____

Andrew G. Campbell
Dean of the Graduate School

Curriculum Vitae

Wenhao Li was born on March 27, 1991 in Jinan, Shandong Province, P. R. China. He earned his Bachelor of Science degree in 2014 at Lanzhou University. He then joined physics department at Brown university as a master's student in 2014 and transferred into the doctoral program after one year at Brown. In 2015 he joined Prof. Rashid Zia's laboratory and started working as a research assistant focusing on the study of carrier transport and structural properties in perovskite materials. He received his Master of Science degree in May, 2017.

Acknowledgements

It has been five years since I started at Brown University. This journey is both fun and challenging. I have so many pleasant memories during this amazing journey and they will be treasures for my life.

First of all I would like to thank my advisor Prof. Rashid Zia for his guidance in the past four years. He sets me a good example of a successful scientist and a supportive mentor. I have learned a lot from his attention to details and his pursuit of perfection. I have been extremely lucky to have Rashid as my advisor.

Secondly I want to thank my labmates Juan David Lizarazo Ferro, Matthew Shao Ran Huang, Wang Yang, and Jonathan Kurvits for their company and help. I have spent more time with them than with my wife in the past four years and they are really important friend to me. Especially, I want to thank David for the valuable discussions and his help with my English writings.

Thirdly I thank my collaborators, Prof. Nitin P. Padture, Srinivas K. Yadavalli, and Yingxia Zong, who have given me great help in sample fabrication. I also want to thank Prof. Alexander Zaslavsky and Dr. Dongfang Li for their helpful discussions and inspirations.

Finally I want to thank my family for their love and support. They offered me care and help in whatever way they could. I would never have completed this journey without them.

This work is dedicated to my family.

Preface

This thesis is based on the following manuscripts and publications:

1. W. Li, S. K. Yadavalli, D. Lizarazo-Ferro, M. Chen, Y. Zhou, N. P. Padture, and R. Zia. "Subgrain special boundaries in halide perovskite thin films restrict carrier diffusion." *ACS Energy Letters* 3, 11, 2669-2670 (2018).
2. W. Li, M. Huang, S. K. Yadavalli, D. Lizarazo-Ferro, Y. Zhou, N. P. Padture, and R. Zia. "Direct Characterization of Carrier Diffusion in Halide-Perovskite Thin Films Using Transient Photoluminescence Imaging" (Accepted.)
3. X. Xiao, W. Li, Y. Fang, Y. Liu, Y. Shao, S. Yang, J. Zhao, R. Zia, and J. Huang "How Charge Carrier Transport Through Ferroelastic Twin Boundaries in Halide Perovskite?" (Submitted.)

The other publications by the author:

1. D. Li, S. Karaveli, S. Cueff, W. Li, and R. Zia. "Probing the combined electromagnetic local density of optical states with quantum emitters supporting strong electric and magnetic transitions." *Physical review letters* 121, 22, 227403 (2018).
2. C. Na, T. Cai, W. Li, K. Hills-Kimball, H. Yang, M. Que, Y. Nagaoka, Z. Liu, D. Yang, A. Dong, C. Xu, R. Zia, and O. Chen. "Yb-and Mn-Doped Lead-Free Double-Perovskite

- Cs₂AgBiX₆ (X= Cl⁻, Br⁻) Nanocrystals." ACS applied materials & interfaces 11, 18, 16855-16863 (2019).
3. D. Ryan A., N. R. Venkatesan, C. J. Dahlman, R. M. Kennard, X. Zhang, W. Li, M. L. Chabinyo, R. Zia, and J. A. Schuller. "Bright magnetic dipole radiation from two-dimensional lead-halide perovskites." (submitted, paper available on arXiv:1901.05136 (2019).)

Contents

List of Tables	xi
List of Figures	xii
1 Introduction	1
1.1 Perovskite Material	1
1.2 Current Research Directions	3
1.2.1 Reduction of Potential Lead Contamination	3
1.2.2 Improvement of Solar Cell Stability	3
1.2.3 Improvement of Solar Cell Fabrication Techniques and Power Conversion Efficiency	4
1.2.4 Studies on Fundamental Properties	4
1.3 Outline	4
2 Stabilization of Mixed-Halide Perovskites by Optical Annealing	6
2.1 Introduction	6
2.1.1 Phase Segregation Mechanisms in $\text{MAPbI}_x\text{Br}_{3-x}$	8
2.1.2 Bandgap Stabilization Methods	8
2.2 Optical Annealing for Bandgap Stabilization	9
2.2.1 PL Spectrum Evolution Under Illumination	9

2.2.2	Improved Photostability after Optical Annealing	11
2.2.3	Optical Annealing Effect Persists for Days	12
2.2.4	Improved Stability Correlated with Increased Lifetime	13
2.3	Possible Mechanism for Phase Segregation and Optical Annealing	14
3	Direct Characterization of Carrier Diffusion in Halide-Perovskite Thin Films	
	Using Transient Photoluminescence Imaging	17
3.1	Introduction	17
3.1.1	Optical Methods for Estimating Carrier Diffusivity	18
3.1.2	Working Principles of Fast-gated Cameras	19
3.1.3	Carrier diffusion and recombination model	20
3.1.4	Crystal Defects	21
3.2	Photoluminescence Imaging Method for Estimating Carrier diffusivity	22
3.2.1	Sample preparation	23
3.2.2	Photoluminescence Imaging in Perovskite thin film	23
3.2.3	Carrier Diffusion and Recombination Model	24
3.2.4	Diffusivity Statistics	26
3.3	Spatial and Temporal PL Spectral Profile	27
3.4	Carrier Diffusion Under Background Illumination	28
3.4.1	Carrier Diffusion Accelerated by Background Carriers	28
3.4.2	Background Carrier Density Estimation	32
3.4.3	Trap Screening Effect by Background Carriers	35
4	Photoluminescence Microscopy for Identifying Sub-grain Boundaries in FAPbI₃	
	Thin Films	37
4.1	Introduction	37
4.1.1	Crystal Boundaries	38

4.1.2	FAPbI ₃ Kikuchi Pattern	39
4.2	Sub-grain Boundary Revealed by Photoluminescence Microscopy	40
4.2.1	Photoluminescence Microscopy for Characterizing Carrier Transport . . .	40
4.2.2	Surface Morphology of Sub-grain Boundary	42
4.3	Crystal Orientations Across Sub-grain Boundaries	46
4.3.1	Electron Backscatter Diffraction	46
4.4	Conclusion	50
5	Charge Carrier Transport in Ferroelastic Twin Boundaries in MAPbI₃ Single Crystals	51
5.1	Introduction	51
5.1.1	Twin Boundaries in MAPbI ₃	52
5.1.2	Polarized Optical Microscopy for Observing Twin domains in MAPbI ₃ . .	53
5.2	Sample Preparation and Characterization	54
5.2.1	Sample Preparation	54
5.2.2	Photoluminescence Imaging Method for Monitoring Carrier Transport . .	55
5.2.3	Confocal Photoluminescence Spectroscopy for Studying Carrier Recombi- nation	59
5.3	Conclusion	60
6	Conclusion	61

List of Tables

3.1	Resulting values for the global fit of the time-resolved PL experiments.	34
4.1	Atomic positions in the unit cell of FAPbI ₃ for Kikuchi pattern simulation as is reported in reference [1]	39

List of Figures

1.1	Cubic perovskite crystal structure. Figure adapted from reference [2] by Green <i>et al.</i>	2
2.1	a. PL spectra of an $\text{MAPbI}_{1.2}\text{Br}_{1.8}$ thin film over 45 s in 5 s increments under 457 nm, 15 mW/cm ² light at 300 K. b. The [200] XRD peak of an x $\text{MAPbI}_{1.2}\text{Br}_{1.8}$ film before (black) and after (red) white-light soaking for 5 minutes at ~ 50 mW cm ² . XRD patterns of an $\text{MAPbI}_{2.4}\text{Br}_{0.6}$ film (dashed green) and an $\text{MAPbI}_{2.1}\text{Br}_{0.9}$ film (dashed brown) are included for comparison. Figures are adapted from reference [3] by Hoke <i>et al.</i>	7
2.2	a. $\text{MAPbI}_{1.3}\text{Br}_{1.7}$ PL spectrum time evolution under 532 nm, 200 mW/cm ² CW laser illumination. b. X-ray diffraction spectrum of a $\text{MAPbI}_{1.3}\text{Br}_{1.7}$ film before (blue), during (cyan), and after (green, yellow, and red) with a 384 nm, 200 mW/cm ² illumination.	10
2.3	a. $\text{MAPbI}_{1.3}\text{Br}_{1.7}$ PL spectrum time evolution under 408 nm, 500 mW/cm ² average power pulsed laser illumination.	11
2.4	PL spectrum time evolution under 532 nm, 100 mW/cm ² CW laser illumination before (a) and after (b) optical annealing.	12
2.5	PL spectrum after 20 min modest power (130 mW/cm ²) 408 nm pulsed laser illumination	13

2.6	a. Schematic diagram of optical annealing cycles. b. PL spectra taken at the end of each annealing cycle. c. PL lifetime spectra at the beginning (N=1) and end (N=20) of the optical annealing sequence. d. In blue the ratio between intensities at 730 and 650 nm, and in red the PL lifetime as a function of optical annealing cycles N.	14
2.7	Predicted phase diagram of the $\text{MAPb}(I_{1-x}\text{Br}_x)_3$ perovskite material. The purple and pink lines are the binodal and spinodal lines, respectively. The dashed horizontal line shows the miscibility gap at room temperature. A thermodynamically stable solid-solution can be formed in the white region. Figure adapted from reference [4] by Brivio <i>et al.</i>	15
3.1	Major components of PIMax 4 camera. Figures are adapted from PIMax 4 manual, page 19. [5]	19
3.2	Working principle of on-CCD accumulation.	20
3.3	The charge transition energy levels of intrinsic defects in FAPbI_3 . Point defects including interstitials ($\text{FA}_i, \text{Pb}_i, \text{I}_i$), vacancies ($\text{V}_{\text{FA}}, \text{V}_{\text{Pb}}, \text{V}_{\text{I}}$) and antisites ($\text{FA}_{\text{Pb}}, \text{Pb}_{\text{FA}}, \text{FA}_{\text{I}}, \text{Pb}_{\text{I}}, \text{I}_{\text{FA}}, \text{I}_{\text{Pb}}$). Figure adapted from Ref. [6].	22
3.4	Time-resolved PL imaging measurements of carrier diffusion. (a) Time resolved PL distribution for 1 ns, 4 ns, 16 ns, and 61 ns time delays after excitation laser pulses. Scale bars are 3 μm . (b) Crosscut of PL distributions and corresponding Gaussian fittings for different time delays. (c) Width of PL distributions fit with a diffusion model, yielding an extracted carrier diffusivity $D = 1.55 \pm 0.02 \text{ cm}^2/\text{s}$	24

3.5	(a) Simulated crosscut of PL distribution (solid lines) and corresponding Gaussian fittings (dotted lines) at 1 ns interval time delays with respect to arrival of the laser pulse, for pump energy density $12.5 \mu\text{J}/\text{cm}^2$. (b) Diffusivities estimated by directly fitting to the simplified diffusion model for the this particular pump energy density. (c) Overestimation of the diffusivity from the ground truth value of $1.20 \text{ cm}^2/\text{s}$ as pump power increases. Red dashed line shows the pump energy density used in the experiment, gray line shows the ground truth value of diffusivity. The overestimation is under 15% for the entire range of carrier concentrations used in the experiment.	25
3.6	Carrier width evolution for different pump powers fitted with the diffusion model.	26
3.7	Diffusivity variation in 20 grains. (a) Width evolution of 20 grains and the corresponding fits to the diffusion model. (b) Histogram of diffusivity D for the 20 grains	26
3.8	Setup for measuring time resolved PL spectral profile.	27
3.9	Transient spatial PL spectral profile at 1 ns (a) and 20 ns (b). (c) PL spectrum for the excited .(d)	28
3.10	Carrier diffusivity enhancement under quasi-CW uniform laser illumination. (a) Schematic illustration of CW illumination and transient PL distribution evolution under different illumination conditions. Scale bars are $3 \mu\text{m}$. (b) Width evolution under different illumination conditions and the corresponding diffusion model fits. The transient PL distribution measurements were taken before applying quasi-CW illumination (blue), with the quasi-CW illumination (yellow), and after turning off the quasi-CW illumination (red). The instantaneous CW illumination power density is $150 \text{ W}/\text{cm}^2$, and the average CW illumination power density is $750 \text{ mW}/\text{cm}^2$. (c) Schematic illustrating the increase in carrier mean free path by charge trap screening effect.	29

3.11	Timing Diagram	30
3.12	Diffusion and recombination kinetics. (a) Diffusivities of three grains as a function of CW illumination power. Inset shows the PL width evolution under various CW illumination powers for grain 1. (b) Transient PL decay at different pump powers fit with a recombination and diffusion model. The decay curves are shifted consecutively by 1 ns for clarity.	32
4.1	Schematic of high-angle boundary, low angle boundary and twin boundary. Figure adapted from publication by Lu et al. [7].	38
4.2	(a) Unit cell structure of α -phase FAPbI ₃ . NH-I hydrogen bonds are shown as dashed lines. Figure adapted from Reference [1]. (b) Simulated Kossel cones for FAPbI ₃	40
4.3	Schematic of push-broom scan setup.	41
4.4	(a) Absorption spectrum, and normalized PL spectra for regions inside the grain (marked in (b) by a circle) and on a grain boundary (marked in (b) with a cross). The black dashed line corresponds to wavelength of 800 nm. (b) PL distribution images for different wavelength ranges reconstructed from the push-broom scan. All scale bars are 2 μ m. Green line corresponds to the excitation spots.	43
4.5	Surface images of FAPbI ₃ perovskite thin film obtained by (a) optical microscopy, (b) SEM, and (c) AFM measurements.	44
4.6	(a-c) Focused excitation PL intensity distributions superimposed onto the SEM image.	44
4.7	(a) PL intensity and (b) PL lifetime maps. All scale bars are 3 μ m. (c-d) Averaged PL intensity and lifetime comparison between boundaries with (Line 1) and without (Line 2) visible grooves.	45
4.8	Time-resolved PL intensity and bi-exponential decay fit.	46

4.9	PL intensity distribution images for four different apparent grains superimposed onto optical microscopy images (a-c) and SEM image (d). Dashed blue lines highlight the special boundaries, and all scale bars are $3\text{ }\mu\text{m}$. Right panels in (d) show EBSD Kikuchi patterns from regions labeled 1-5.	47
4.10	(a) Raw SEM image. (b) Rotated and scale-corrected SEM image. (c) Optical microscopy image. All scale bars are $3\text{ }\mu\text{m}$	48
4.11	Kikuchi pattern fitting for (a) region 1-4 and (b) region 5. The label are the Miller index for a plane.	49
4.12	(a-b) Subgrain boundaries with turning points. (c) Two subgrain boundaries intersect.	49
5.1	a. Bright-field TEM image of a pristine MAPbI_3 thin film. A stripe contrast is visible through some of the grains. Scale bar is 500 nm. b. Diffraction pattern taken from a grain exhibiting stripe contrast showing two single-crystal patterns with a mirrored relationship. Figure adapted from reference [8]	52
5.2	Polarized light microscopy image of MAPbI_3 single crystal. The bright and dark regions correspond to different ferroelastic domains in the MAPbI_3 single crystal sample.	54
5.3	Permissible domains of the MAPbI_3 tetrahedral phase. At the cubic-to-tetrahedral transition, the tetrahedral unit cell can form with the c axis aligned along any of the three axes (x, y, and z) of the parental cubic phase, leading to three possible configurations (X, Y, and Z). The six possible domain orientations that are characterized by domain walls intercepting at 0° , 90° , or 45° in the principal planes of the parental phase and at 70° and $\approx 110^\circ$ in the (110) plane. Figure adapted from reference [9].	55

5.4	(a) PL imaging under CW laser excitation; (b) PL imaging under pulsed laser excitation ($120 \mu\text{J}/\text{cm}^2$); (c) PL intensity distribution cross-cut along the white dashed line shown in (a) & (b). Scale bars are $2 \mu\text{m}$	56
5.5	Comparison of carrier transport across FTBs and grain boundaries via photoluminescence (PL) imaging. (a) Optical microscopy image and (b) the corresponding PL intensity image of a MAPbI_3 multi-crystal sample with GBs. The PL excitation position is indicated by the blue point. (c) Polarized optical microscopy image and (d) the corresponding PL intensity image of a MAPbI_3 single crystal sample with a TB.	57
5.6	The proposed energetic diagram of MAPbI_3 with GBs (left panel) or FTBs (right panel) exhibiting the origin of their different impacts on charge carrier transport and recombination.	58
5.7	Impact of FTBs on charge carrier recombination probed scanning confocal microscopy. Confocal PL intensity mapping (a) and lifetime mapping (b) of FTBs. (c) Time-resolved PL intensity data and (d) single exponential fitting overlayed on the 15 ns to 90 ns time range.	59

Chapter 1

Introduction

1.1 Perovskite Material

In recent years, organic-inorganic halide perovskites (OIHP) have attracted significant attention due to their application in solar cells and other optoelectronic devices. The rapidly increasing power conversion efficiency of OIHP solar cells has recently exceeded 24%. [10]. Perovskite materials have a crystal structure that can be described by the chemical formula ABX_3 , where A and B are 12- and 8-coordinates cations, and X is the anion [2] as is shown in Fig. 1.1. Possible combinations of A, B and X are restricted by charge balance and their relative atomic/molecular sizes. Perovskite single crystals usually have orthorhombic, tetragonal or cubic structures. The most favorable choices for A in solar cells are Cs, CH_3NH_3 (methyllumonium or MA for short), $HC(NH_2)_2$ (formamidinium or FA for short); for B choices are Pb and Sn; and for the anion X I, Br, Cl can be used. Furthermore, A, B, and X can also be taken as compounds which provides rich combinations of chemical compositions; for example, one of the OIHP solar cells with the highest power conversion efficiency of 21% has the perovskite absorber $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$. [11]

OIHPs such as $MAPbI_3$ and $FAPbI_3$ have many favorable properties for solar cell applications

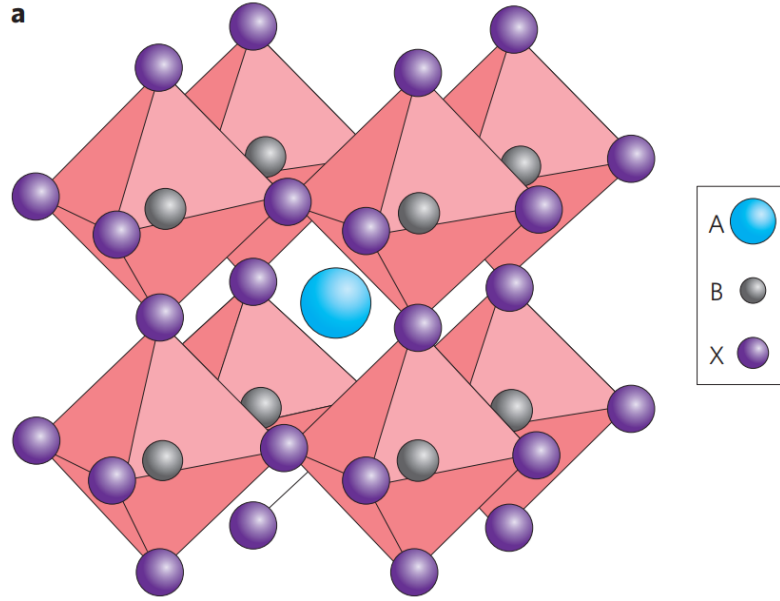


Figure 1.1: Cubic perovskite crystal structure. Figure adapted from reference [2] by Green *et al.*.

such as a high absorption coefficient, high quantum efficiency, and suitable bandgap. Due to the high absorption coefficient, the OIHP layer in solar cells can be made as thin as 500 nm and still absorb most of incident sunlight, this is much thinner than single crystal silicon solar cells which require thicknesses ranging from 100 μm to 500 μm . Furthermore, the bandgap of perovskite materials can be tuned to achieve a desirable value for solar energy harvesting by using compounds for A, B, and X. A tuneable bandgap is a favorable property for designing both single junction and tandem solar cells. OIHP solar cells are also much cheaper than the silicon solar cells and can be manufactured by simple solution processing.

On the other hand, OIHP materials have some issues that need to be solved before they can come out of the lab. They have poor stability and homogeneity; they usually contain the poisonous element lead (Pb); and they are sensitive to moisture and high temperature. Encapsulation could solve some of these, but even if the encapsulation can be good enough to protect the perovskite layer from moisture, it could still be degraded due to temperature increases and light-induced ion migration. Ion migration occurs in many perovskite materials, for example,

in the mixed halide perovskite material $\text{MAPbI}_x\text{Br}_{3-x}$, where it induces segregation into I-rich and Br-regions (phase segregation) and leads to a drop in open circuit voltage. Another issue is that in large ($> 60 \text{ cm}^2$) solar cells the power conversion efficiency (PCE) is only 16.4% whereas for small area devices PCE has been found as high as 24%; this is partly due to the fact that the spin-coating method that produces the small high-quality perovskite films renders large solar cells with poor homogeneity. Furthermore, an environmental concern is that the lead contained in some of these perovskite solar cells might leak into the environment.

1.2 Current Research Directions

Recent research on perovskite materials can be categorized into the following groups:

1.2.1 Reduction of Potential Lead Contamination

Because the presence of Pb is not necessarily a problem if it is well encapsulated within the solar cell module and recycled by the end of the solar cell lifetime, one way of reducing the risk of Pb exposure is to develop suitable encapsulation techniques. Another option is to substitute Pb with other elements such as another group 14 metal. However, it has been theoretically predicted that halide perovskites based on Pb or Sn are the best choices in terms of optoelectronic properties. [12] This makes Sn the most favorable candidate for substituting Pb; however, Sn-based solar cell devices have a relatively low power conversion efficiency of around 8%. [13]

1.2.2 Improvement of Solar Cell Stability

Since perovskite materials are sensitive to moisture and oxygen, one way of improving the life-time of perovskite solar cells is to prevent the perovskite layers from being exposed to air by encapsulation. It has been shown that a perovskite solar cell device with good encapsulation can tolerate continuous light illumination for more than 500 hours without a drop in efficiency. [14]

With regard to intrinsic thermal stability and ion migration issues, these have been shown to be possible to reduce by composition engineering. [15, 16]

1.2.3 Improvement of Solar Cell Fabrication Techniques and Power Conversion Efficiency

The quality of perovskite absorbing layers is a very important factor for determining the performance of perovskite solar cells. High-quality perovskite films are characterized by having high crystallinity, low defect density, and smooth surface morphology, which largely depend on sample composition and fabrication method. Currently available fabrication and processing methods include: one-step deposition, solvent engineering, doctor blade, solvent annealing, chemical vapour deposition, and thermal vapour deposition. [17–19] The fast increase of power conversion efficiency of perovskite solar cells in recent years is mostly due to composition engineering and improving fabrication techniques.

1.2.4 Studies on Fundamental Properties

The studies of fundamental perovskite materials properties lags behind the fast engineering development in solar cell applications. Perovskite materials exhibit many interesting and unique structural and optoelectronic properties that are not well understood and characterized yet. Our research focuses on the study of the optoelectronic and structural properties of OIHPs, which could ultimately assist in the development of improved solar cells.

1.3 Outline

In this thesis, we present photoluminescence spectroscopy methods for studying the structural and optoelectronic properties of perovskite materials. Specifically, this thesis will be structured as follows.

In Chapter 2 we present the observation of an optical annealing effect in mixed-halide $\text{MAPbI}_x\text{Br}_{3-x}$ perovskite materials that improves the optical quality and photostability. Currently the phase segregation mechanism of this group of materials is still debated and the effect we observed provides a new observation for evaluating the available phase segregation mechanisms. However, we could not reproduce this effect on all samples reliably. This issue with reproducibility prevented us from fully understanding the mechanism of the observed effect, and then we turned to study more robust phenomena in perovskite materials as shown in the following chapters.

In Chapter 3 we developed a time-resolved photoluminescence imaging method for studying carrier diffusion in FAPbI_3 perovskite thin films. This method allows transient PL imaging with a diffraction limited spatial resolution (~ 300 nm) and a sub-nanosecond (500 ps) temporal resolution to directly observe carrier diffusion and reliably estimate diffusivity. Combining this method with background continuous-wave illumination, carrier diffusivity was found to increase with the background carrier density. This effect is discussed within the context of trap-carrier interactions.

In Chapter 4 we used photoluminescence microscopy to reveal sub-grain special boundaries in FAPbI_3 perovskite thin films. These sub-grain special boundaries restrict carrier diffusion and serve as non-radiative recombination sites. However, these sub-grain boundaries, which cannot be observed by conventional AFM or SEM measurements, may explain why the performance of perovskite solar cells has not scaled with apparent grain size.

Finally, in Chapter 5 we study carrier transport and recombination on ferroelastic twin boundaries in MAPbI_3 . Different from the grain boundaries and the sub-grain boundaries discussed in the previous chapters, the ferroelastic twin boundaries are found not to impede carrier transport nor to introduce non-radiative recombination channels.

Chapter 2

Stabilization of Mixed-Halide

Perovskites by Optical Annealing

2.1 Introduction

Mixing compounds, rather than pure perovskite compounds, is usually required for overcoming thermal or structural instabilities in perovskite thin films, and also for tuning the bandgap required for energy harvesting. In addition, mixed-halide perovskites can be used as front cells in tandem solar cell structures and boost the efficiency of commercial silicon photovoltaic solar cells thanks to their continuously tunable bandgap. Power conversion efficiency of more than 30% is predicted theoretically for a front perovskite cell with a suitable wide bandgap (1.7 ~ 1.8 eV).

Several groups have demonstrated that the bandgap of mixed-halide $\text{MAPbI}_x\text{Br}_{3-x}$ can be continuously tuned by changing the I to Br ratio. [3, 20] However, higher bandgap materials do not exhibit the high open-circuit voltages required for useful solar cells. Furthermore, Hoke *et al.* showed that even though the bandgap can be tuned from 1.6 to 2.3 eV, the mixed-halide $\text{MAPbI}_x\text{Br}_{3-x}$ is not stable under illumination and will phase-segregate into I-rich and Br-rich

regions, which drops the open-circuit voltages. [3] Figure 2.1 from Hoke *et al.* [3] shows how the PL and XRD spectra change under illumination; before illumination the PL spectrum has a single peak around at 670 nm (1.85 eV) and corresponds to the mixed-state of iodine and bromine; then, as the sample is further illuminated a sub-bandgap peak appears at 740 nm (1.67 eV) which corresponds to the I-rich regions. (The Br-rich regions are not evidenced in the PL spectrum because of band alignment between the I-rich and Br-rich regions. [21]) This figure also shows how the XRD spectrum changes under illumination. Initially there is a single peak indicative of the mixed state, and after illumination there are now contributions from both I-rich and Br-rich regions.

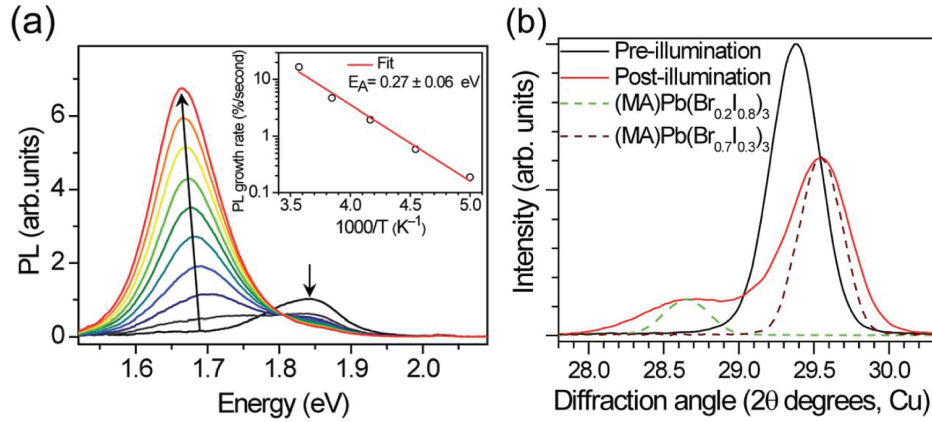


Figure 2.1: a. PL spectra of an $\text{MAPbI}_{1.2}\text{Br}_{1.8}$ thin film over 45 s in 5 s increments under 457 nm, 15 mW/cm^2 light at 300 K. b. The [200] XRD peak of an $x \text{MAPbI}_{1.2}\text{Br}_{1.8}$ film before (black) and after (red) white-light soaking for 5 minutes at $\sim 50 \text{ mW cm}^2$. XRD patterns of an $\text{MAPbI}_{2.4}\text{Br}_{0.6}$ film (dashed green) and an $\text{MAPbI}_{2.1}\text{Br}_{0.9}$ film (dashed brown) are included for comparison. Figures are adapted from reference [3] by Hoke *et al.*

In this chapter, we present observations of increased photostability of a mixed-halide perovskite $\text{MAPbI}_{1.3}\text{Br}_{1.7}$ after illumination with a strong pulsed laser. If reproducible and reliable, this effect could be turned into a useful processing technique for the stabilization of mixed-halide perovskites. However, after reproducing it in several occasions, and while trying to further investigate its nature, the conditions necessary to observe it again could not be satisfied. The tested samples were prepared with the same recipe and optically annealed under the same illumination

conditions, but only a fraction of samples showed the improved stability. We speculate that this variation could be related either to unconsidered sample fabrication details or to the humidity level during the optical annealing process which lacks good control.

2.1.1 Phase Segregation Mechanisms in $\text{MAPbI}_x\text{Br}_{3-x}$

Several theoretical and experimental studies have been done to unravel the nature and mechanisms of phase segregation in $\text{MAPbI}_x\text{Br}_{3-x}$ thin films. Using density functional theory, Brivio *et al.* made a thermodynamic analysis of the $\text{MAPbI}_x\text{Br}_{3-x}$ perovskite material. [4] In their analysis the authors constructed the phase diagram and identified a miscibility gap, which refers to a range of compositions in which the mixed halide perovskite would segregate into I- and Br-rich regions through binodal spinodal decomposition. Using nanoscale imaging and multiscale modeling, Bischak *et al.* showed halide phase segregation produces ~ 8 nm iodide-rich clusters that can be induced by the interaction of photo-excited charges with the lattice. [22] Barker *et al.* reported that ion segregation, which creates iodide-rich, low-bandgap regions close to the illuminated surface of the film, can be promoted by halide defects. Furthermore, they conducted an experiment where phase segregation was reduced by illuminating the sample from top and bottom at the same time, which led them to propose that a strong gradient in the carrier generation rate (which is large in perovskites given their strongly absorbing nature) gives rise to phase segregation. [23]

While the above models explain some features of phase segregation, no theory explains all the phenomena related to phase segregation in the mixed-halide $\text{MAPbI}_x\text{Br}_{3-x}$ perovskite materials.

2.1.2 Bandgap Stabilization Methods

Besides studying the mechanism of phase segregation, researchers are also looking for ways to stabilize the bandgap of mixed-halide perovskite materials. For example, Zhibin *et al.* [24] used X-ray diffractometry and transient absorption spectroscopy to show that the I/Br mixed state

can be stabilized by partially replacing lead with tin. In these phase-stabilized films the bandgap can be continuously tuned from 1.35 eV to 2.03 eV for this group of perovskite materials. The optical annealing method that we will introduce here can potentially be further developed into a bandgap stabilization method for the mixed halide perovskites.

2.2 Optical Annealing for Bandgap Stabilization

2.2.1 PL Spectrum Evolution Under Illumination

The samples used for studying phase segregation in $\text{MAPbI}_x\text{Br}_{3-x}$ were prepared using a solvent engineering method [25] in which an anti-solvent is dripped into the film while spin coating to quickly extract the solvent and form films with good crystallinity. Figure 2.2a shows the PL spectrum evolution within 20 minutes when the sample is illuminated with a 200 mW/cm², 532 nm CW laser. In the initial mixed state, a single PL peak near 650 nm is observed, and the corresponding bandgap E_g of 1.9 eV can be related to a composition x using the following phenomenological equation taken from reference [26].

$$E_g(x) = 1.57 + 0.13x + 0.0367x^2. \quad (2.1)$$

After several minutes of illumination, a second peak emerges near 730 nm (consistent with a 1.7 eV bandgap for $\text{MAPbI}_{2.2}\text{Br}_{0.8}$) which corresponds to segregation into I-rich regions. The intensity of the sub-bandgap peak quickly grows over a matter of minutes and then stabilizes. Figure 2.2b shows how the phase segregation is reversible, because the sub-bandgap peak disappears after the sample is left in dark for around 30 minutes.

The reversible nature of the observed phase segregation was also evidenced by X-ray diffraction as shown in Fig. 2.2b. Under a modest illumination of 200 mW/cm², the initial single XRD peak (shown in black) splits into two peaks corresponding to the I-rich and Br-rich phases. Then after the sample is left in dark for 30 minutes the initial XRD spectrum (blue) is mostly recovered

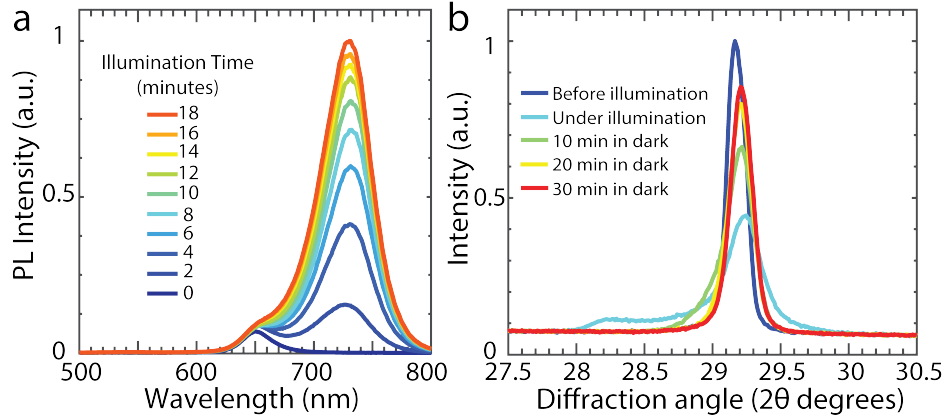


Figure 2: a. MAPbI_{1.3}Br_{1.7} PL spectrum time evolution under 532 nm, 200 mW/cm² CW laser illumination. b. X-ray diffraction spectrum of a MAPbI_{1.3}Br_{1.7} film before (blue), during (cyan), and after (green, yellow, and red) with a 384 nm, 200 mW/cm² illumination.

(red).

We then studied phase segregation induced by pulsed-laser illumination. Figure 2.3 shows the PL spectrum evolution under the illumination of a pulsed laser (wavelength 408 nm, average power of 500 mW/cm², pulse width of 180 ps, and 40 MHz repetition rate). It was found that a higher average power produces a qualitatively different change in how the PL spectrum evolves with time. After the 730 nm peak (associated with the I-rich region) emerges, continued illumination leads to a decrease in its intensity as well as a strong increase in the original 650 nm peak (associated with the initial mixed state).

Conventionally, a light-induced sub-bandgap peak stabilizes under illumination, and the phase segregated sample needs a dark environment to return to its initial mixed state. But here, the peak for the mixed state rises under illumination, and at the same time the sub-bandgap mostly disappears. We will subsequently refer to this process as optical annealing. Furthermore, as we will show in the next section, this optical annealing process makes the samples resistant to photo segregation.

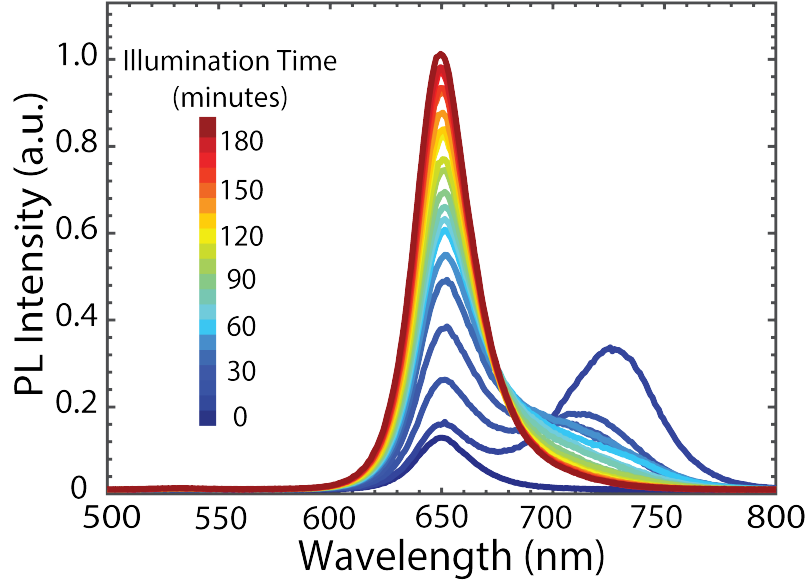


Figure 2.3: a. MAPbI_{1.3}Br_{1.7} PL spectrum time evolution under 408 nm, 500 mW/cm² average power pulsed laser illumination.

2.2.2 Improved Photostability after Optical Annealing

To study this optical annealing, we compared the photostability of MAPbI_{1.3}Br_{1.7} samples before and after optical annealing with a high average power (1 W/cm²) pulsed laser. The optical annealing process used for this study consisted of 21 cycles of illumination for intervals of 10 minutes followed by 15 minutes of darkness (schematic diagram of this is shown in Fig. 2.6a). PL spectra for the sample before and after annealing were acquired under modest (100 mW/cm²) illumination to determine the change in level of photosegregation.

Whereas the spectrum of the sample with no applied optical annealing shows the emergence of an I-rich peak near 730 nm within 20 minutes, the sample after optical annealing shows a very stable and bright peak at 650 nm (consistent with the original mixed composition), as is shown in Fig. 2.4.

Besides the increased photostability, the sample is about 10X brighter after optically annealing. Also, in opposition to what occurs in samples with no optical annealing, no increase in PL intensity is observed under illumination. This suggests an improvement in optical quality (as will

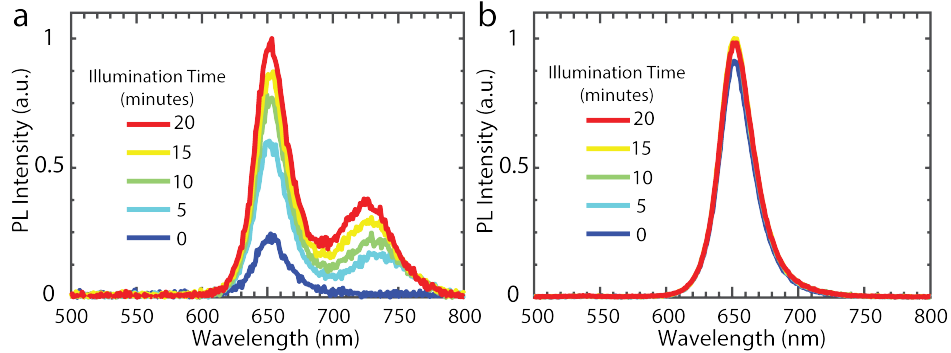


Figure 2.4: PL spectrum time evolution under 532 nm, 100 mW/cm² CW laser illumination before (a) and after (b) optical annealing.

be shown with PL lifetime studies). We tested the optical annealing effect on a range of samples, and found that the condition for such annealing is a relatively high average power pulsed laser illumination (for our case 408nm, 180 ps pulse width, 40 MHz repetition rate, average power is in the range of 300 mW/cm² to 1500 mW/cm²).

2.2.3 Optical Annealing Effect Persists for Days

The increased photostability and optical quality are appealing properties for perovskite solar cell applications. For this purpose, it is important to know how long this optical annealing effect persists. Therefore we tested the photostability of an optically annealed sample during several days.

An optically annealed sample was sealed in nitrogen-filled foil bags and taken out for testing everyday. Each day it was illuminated with modest power (130 mW/cm²) 408 nm pulsed laser for 20 minutes and then the PL spectrum was acquired to study the photostability. As is shown in Figure 2.5, the PL spectrum remained stable for four days with only a small intensity decrease after the first day. Most importantly, given that there is a single peak at around 650 nm these spectra correspond to the mixed state, because had there been segregation a second peak would have arisen at around 730 nm as occurs in Fig. 2.2a. This experiment shows that the increased photostability can persist for at least four days. This experiment stopped after four days because

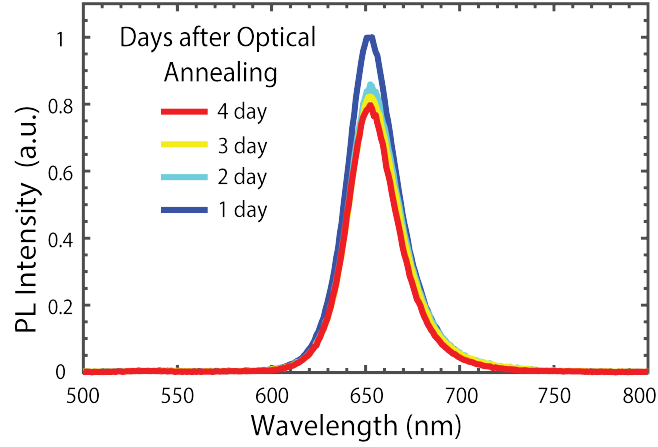


Figure 2.5: PL spectrum after 20 min modest power (130 mW/cm^2) 408 nm pulsed laser illumination

the sample was unfortunately damaged during a SEM measurement.

2.2.4 Improved Stability Correlated with Increased Lifetime

The optical annealing process was split into a sequence of smaller annealing cycles to study its progressive effect. One annealing cycle consisted of 10 minutes illumination with a 408 nm pulsed laser (average power of 1 W/cm^2) followed by 15 minutes of dark treatment. (The dark treatment is to ensure the sample returns to a mixed state.) To highlight the change in photostability, PL spectra were taken at each cycle right after the 10 minutes of illumination (yellow markers in Fig. 2.6a). To study the lifetime spectra of the mixed state, we took the PL lifetime spectrum at the beginning of each cycle (blue markers in Fig. 2.6b)

As is shown in Fig. 2.6b, at the end of the first annealing cycle, a segregated peak appears centered around 730 nm. In the following cycles, the intensity of this segregated peak decreases. The ratio of PL intensity at 730 nm and 650 nm decreases (and almost vanishes) with annealing cycle as shown in Fig. 2.6d. At each cycle, the PL decay curves were fitted to a bi-exponential model and the weighted PL lifetime increased from 19 ns to 68 ns.

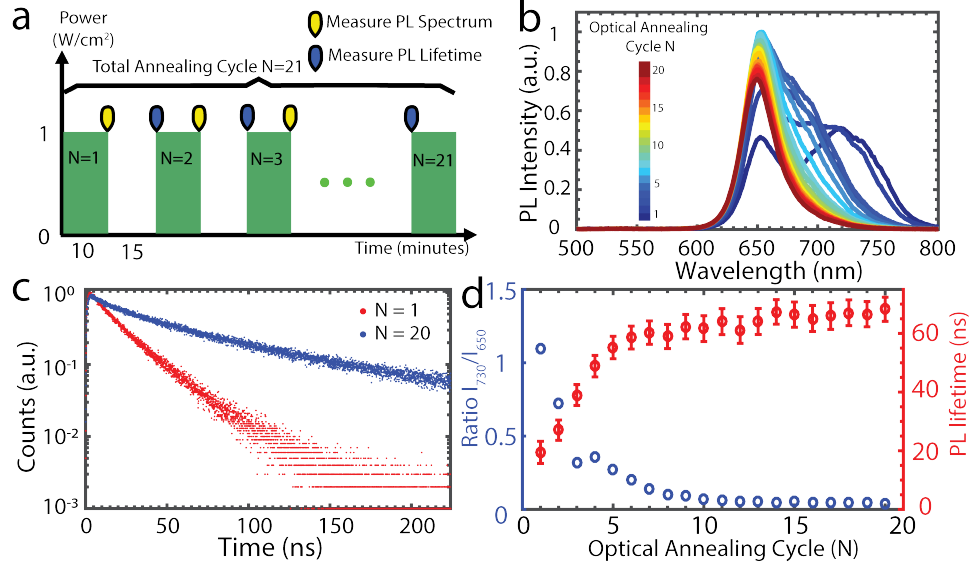


Figure 2.6: a. Schematic diagram of optical annealing cycles. b. PL spectra taken at the end of each annealing cycle. c. PL lifetime spectra at the beginning (N=1) and end (N=20) of the optical annealing sequence. d. In blue the ratio between intensities at 730 and 650 nm, and in red the PL lifetime as a function of optical annealing cycles N.

2.3 Possible Mechanism for Phase Segregation and Optical Annealing

The optical annealing effect provides an additional observation for studying the phase segregation of mixed-halide $\text{MAPbI}_x\text{Br}_{3-x}$ perovskite material. We will try to evaluate the currently proposed mechanisms based on our new observation. As is shown in Fig. 2.3, the PL spectrum evolution indicates that the $\text{MAPbI}_{1.3}\text{Br}_{1.7}$ sample went through mixed-segregated-mixed states under high power illumination (500 mW/cm^2).

Brivio *et al.* [4] considered the $\text{MAPbI}_{1.3}\text{Br}_{1.7}$ to be in a meta-stable state from which phase segregation occurs by binodal spinodal decomposition. The predicted phase diagram is shown in Fig. 2.7. Illumination is considered a perturbation that triggers the mixed halide perovskite to decompose and form thermodynamically stable I- and Br-rich regions. This model successfully predicts the position of the sub-bandgap peak, but cannot explain the I and Br remixing under

dark environment or under high power illumination.

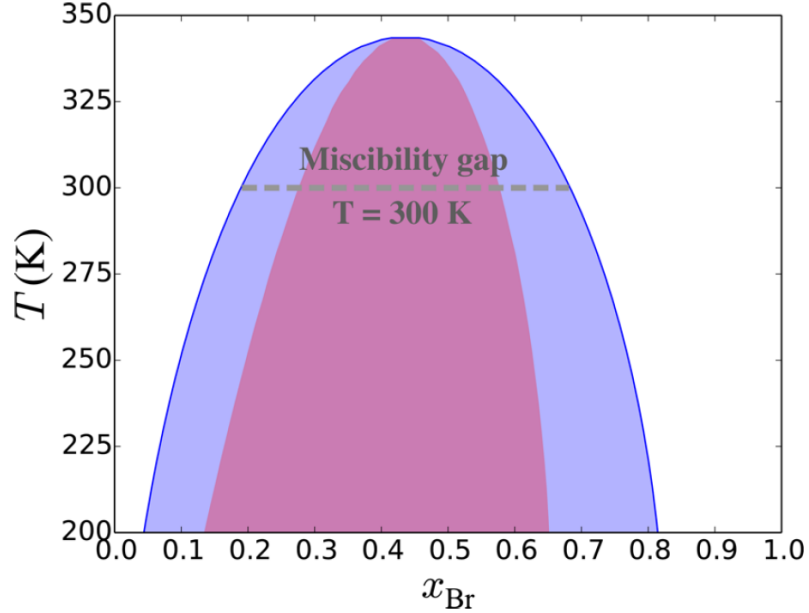


Figure 2.7: Predicted phase diagram of the $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite material. The purple and pink lines are the binodal and spinodal lines, respectively. The dashed horizontal line shows the miscibility gap at room temperature. A thermodynamically stable solid-solution can be formed in the white region. Figure adapted from reference [4] by Brivio *et al.*.

Both the theories of Barker [23] and Bischak [4] consider the photo excited electrons as the catalyst for phase segregation, and successfully explain both segregation under illumination and the I and Br remix under a dark environment. However, these two theories predict that phase segregation would be enhanced by a high illumination power (in our case $500 \text{ mW}/\text{cm}^2$), which does not agree with our observations regarding the optical annealing effect as seen in Fig 2.3.

As is shown in Fig. 2.6d, the PL lifetime increases along with the improvement of photostability. The longer lifetime indicates a decrease of non-radiative recombination pathways, and this suggests that the optical annealing reduces defect densities, which in turn could decrease phase segregation. Reduction of defects might lead to a mixed state that is energetically favorable under illumination, thus removing the driving force for phase segregation.

However, a complete understanding of the optical annealing mechanism is still lacking. In our

experiments samples prepared with the same recipe did not show the same increase in stability. One possible reason for the low reproducibility is that the quality of the samples is hard to control. The samples are prepared with a solvent engineering method where small changes in the fabrication process (such as the glovebox environment, the dripping time, and the dropping speed of the anti-solvent) can greatly affect the sample quality. Another reason might be related to a poor control of humidity during the optical annealing process. Failing to reproduce this optical annealing effect reliably, we turned to study more robust behaviors in perovskite materials.

Chapter 3

Direct Characterization of Carrier Diffusion in Halide-Perovskite Thin Films Using Transient Photoluminescence Imaging

3.1 Introduction

Despite the fast increase in PCE achieved through improvements in fabrication processes and compositional engineering, the underlying optoelectronic properties of perovskite materials, including charge transport, remain controversial. In particular, a better understanding of intrinsic properties could help elucidate the fundamental limits of perovskite thin-film solar cells, and help establish guidelines for their further development.

Charge transport properties are of great relevance to optoelectronic devices, as they determine

the quantum efficiency of both photovoltaics and light-emitting diodes. In such devices, the mobility of charge carriers can be limited by both extrinsic and intrinsic factors [27]. Intrinsic factors, such as charge-lattice interactions, cannot be avoided, but extrinsic factors, such as crystal defects and grain boundaries, are qualities that can be engineered to enhance device performance. To study charge-transport properties experimentally, several electrical [28–32] and optical methods [33–47] have been developed to measure carrier diffusivity and mobility.

In this chapter, we first give an overview of the optical methods and instruments used for estimating carrier diffusivity. After this introduction, a model for describing carrier diffusion and recombination will be presented, and also the possible crystal defects in FAPbI₃ and their energy levels will be briefly discussed. We then present a transient PL imaging method that enables direct characterization of carrier diffusion and use it for the study of FAPbI₃ thin films. This method estimates carrier diffusivity by recording with nanosecond resolution the PL distribution that results from injecting carriers with a pulsed laser. We also present an elaboration of this method, which adds a background carrier density with help of continuous-wave illumination, and show that in the case of FAPbI₃ this addition gives rise to an increase in carrier diffusivity. This increase in diffusivity is discussed within the context of trap-carrier interactions.

3.1.1 Optical Methods for Estimating Carrier Diffusivity

Optical methods for characterizing carrier diffusivity can be divided into three categories: transient absorption spectroscopy [38, 39], light-induced transient grating spectroscopy [40–43], and transient photoluminescence (PL) spectroscopy [44–47]. In the former two categories, the changes in light absorption and diffraction efficiency require a high carrier concentration ($\sim 10^{17} \text{ cm}^{-3}$ to 10^{19} cm^{-3}). However, carrier concentration drops quickly with time due to diffusion and recombination, which limits the spatial and temporal window for observing carrier diffusion. Transient PL spectroscopy, on the other hand, can help monitor carrier concentrations over longer time scales. However, conventional time-resolved PL setups with discrete detectors (e.g. avalanche

photodiodes or photo-multiplier tubes) generally only measure the transient PL at one location on the sample, and require repeated measurements at multiple positions to monitor carrier diffusion. The accuracy of such methods can be compromised if the measured locations on the sample are too few; conversely, scanning measurements across the sample may take a long time and may be impacted by sample degradation.

3.1.2 Working Principles of Fast-gated Cameras

Unlike conventional time-resolved PL setups, a fast gated intensified camera (PIMax 4, Princeton Instrument) was used to record transient PL images. This type of camera includes a photocathode, a microchannel plate, a phosphor, a fiber-optic bundle, and a CCD array as shown in Fig. 3.1. In order to achieve sub-nanosecond resolution, incident photons are converted to electrons and gated with high voltage pulsed.

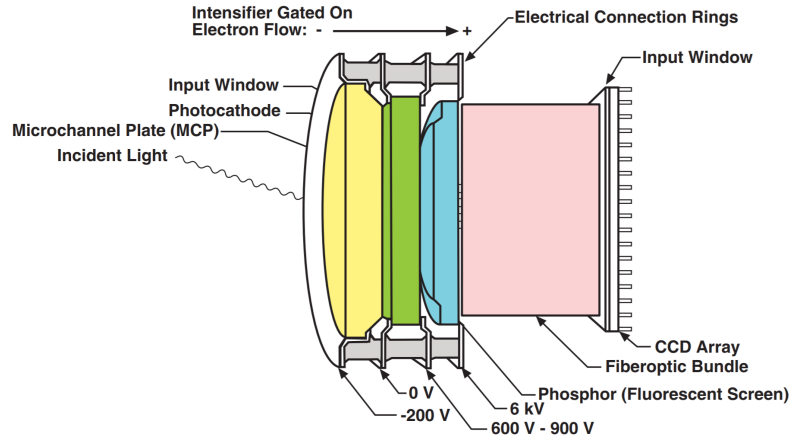


Figure 3.1: Major components of PIMax 4 camera. Figures are adapted from PIMax 4 manual, page 19. [5]

When the intensifier is gated ON, the electrons produced in the photocathode will be attracted to and accelerated in the microchannel plate (MCP). Furthermore, if electrons hit the channel walls, additional electrons will be generated, resulting in an electron gain that can be adjusted by tuning the accelerating voltage of the MCP. When the electrons leave the MCP, they are further

accelerated and strike a phosphor, where one electron generates multiple photons. Because of the gain mechanisms, now many photons will reach the CCD for each of the photons that initially struck the photocathode. The photons are transferred to the CCD with a fiber bundle and become electrons trapped in the CCD pixels where they accumulate until read out.

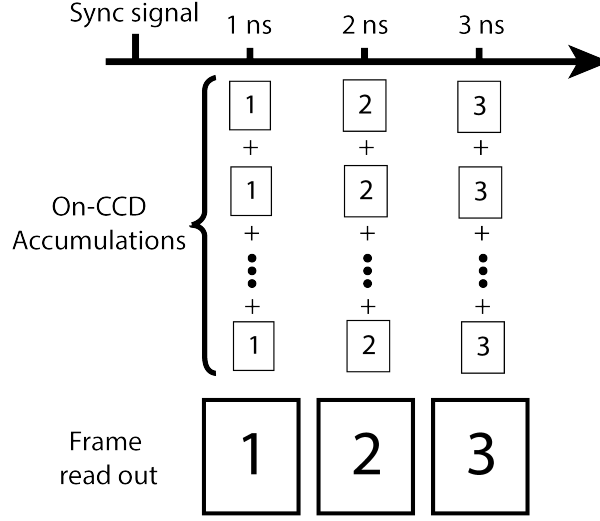


Figure 3.2: Working principle of on-CCD accumulation.

To further increase the signal to noise ratio, the camera provides a binning mechanism called on-CCD accumulation to record events that happen repetitively. The operating principle relies on repeated measurements at the same time delay with respect to the sync signal. The electrons from each exposure are stored in the CCD pixels and are read out all at once after the last exposure. This on-CCD accumulation is better than software binning since it avoids unnecessary readout noise.

3.1.3 Carrier diffusion and recombination model

In order to describe the carrier diffusion and recombination in perovskite thin films, a diffusion term is introduced into the Shockley-Hall-Read recombination model [38]:

$$\frac{\partial n(x, y, t)}{\partial t} = D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) n(x, y, t) - \frac{1}{\tau} n(x, y, t) - \beta^* n(x, y, t)^2, \quad (3.1)$$

where D is the carrier diffusivity assuming isotropic diffusion, τ is the carrier lifetime, and β^* is bimolecular recombination coefficient. The linear recombination $-\frac{1}{\tau}n(x, y, t)$ term corresponds to the trap-assistant recombination, and the bimolecular recombination term $-\beta n(x, y, t)^2$ corresponds to electron and hole inter-band recombination.

If only considering the carrier diffusion in 2D with no recombination, the equation for diffusion in two dimension reads:

$$\frac{\partial n(x, y, t)}{\partial t} = D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) n(x, y, t).$$

Then carrier concentration n has a simple solution

$$n(x, y, t) = \frac{1}{2(\pi Dt)^{\frac{1}{2}}} e^{-\frac{x^2}{4Dt}},$$

and the width of carrier distribution follows a simple model $\sigma = \sqrt{2Dt}$. Note that this model is also valid if the linear recombination term is added to diffusion equation. But there is no simple solution if second- or higher-order decay terms exist. In this chapter, the carrier diffusivity is estimated by fitting the carrier distribution width evolution with $\sigma = \sqrt{2Dt}$. The systematic error in diffusivity estimation induced by using this model will be estimated numerically later in this chapter.

3.1.4 Crystal Defects

Perovskite crystals can have point defects including vacancies as well as interstitial and substitutional atoms. It is important to know the defect energy levels in the bandgap. If an electron gets captured by a shallow defect and re-emitted into conduction band, the electron density in the conduction band would not change. However, if an electron is captured by a deep-energy-level defect, it will lower the free carrier density, and may a high probability of nonradiative recombination.

In FAPbI₃ perovskite materials, several kinds of intrinsic defects exist with different energy

levels. Liu *et al.* theoretically predict the intrinsic point defect levels in FAPbI_3 with first-principles calculations as is shown in Fig. 3.3. [6]

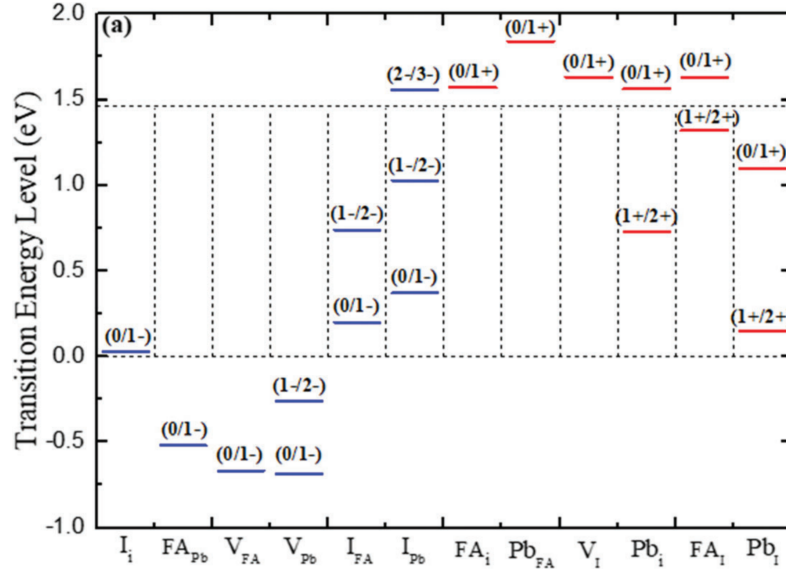


Figure 3.3: The charge transition energy levels of intrinsic defects in FAPbI_3 . Point defects including interstitials (FA_i, Pb_i, I_i), vacancies (V_{FA}, V_{Pb}, V_I) and antisites ($FA_{Pb}, Pb_{FA}, FA_I, Pb_I, I_{FA}, I_{Pb}$). Figure adapted from Ref. [6].

3.2 Photoluminescence Imaging Method for Estimating Carrier diffusivity

Here, we present a wide-field transient PL imaging method for estimating carrier diffusivity that allows temporal binning with sub-nanosecond (500 ps) resolution. Compared with conventional transient PL spectroscopy, this method replaces the point detector with a megapixel intensified camera that parallelizes the measurement to achieve diffraction-limited resolution (~ 300 nm) over a wide observation field ($\sim 130 \mu\text{m}$). By repeatedly gating the intensifier at fixed-time intervals after the laser excitation pulses, this camera can be used to build up a high signal-to-noise image for a given delay time. The high temporal and spatial resolutions as well as short measurement time allows us to explore carrier diffusion under various conditions. We studied carrier diffusion

within individual grains of this material to preclude the confounding effect of grain and sub-grain boundaries that will be explored in chapter 4.

3.2.1 Sample preparation

In particular, we study carrier diffusion in formamidinium lead triiodide (FAPbI₃) perovskite thin films. FAPbI₃ is a popular perovskite solar cell absorber due to its good thermal stability and desirable bandgap of 1.45 eV. Solar cells with a FAPbI₃ absorber with greater than 20% efficiency have been reported [48]. Large-grain ($\sim 5 \mu\text{m}$) thin films can also be fabricated by using a solvent annealing method [49].

3.2.2 Photoluminescence Imaging in Perovskite thin film

To characterize carrier diffusion, samples were excited by a focused 408 nm pulsed laser. Spatially resolved PL was acquired and imaged onto a fast-gated intensified camera (Princeton Instruments, PI-MAX4). Exposures of 1 ns (using the picosecond gating configuration) were repeated for 6.4×10^5 cycles at the same delay time with respect to excitation laser pulses (10 kHz repetition rate).

The PL images, recorded as a function of time delay with respect to the excitation laser pulses, are shown in Fig. 3.4a. The PL distribution expands with time and keeps an approximate 2D-Gaussian shape until it is limited by grain boundaries. Note that this expansion rate cannot be due to light traveling and scattering in the material, because that process would occur at much faster timescales. The slow expansion rate and the barriers observed at grain boundaries (as seen in the rightmost panel) indicate that the PL distribution dynamics are related to carrier diffusion in the material. Carriers generated in the illuminated region (near-diffraction-limited, 250 nm spot) diffuse due to the carrier-concentration gradient, and ultimately decay through radiative and non-radiative recombination channels.

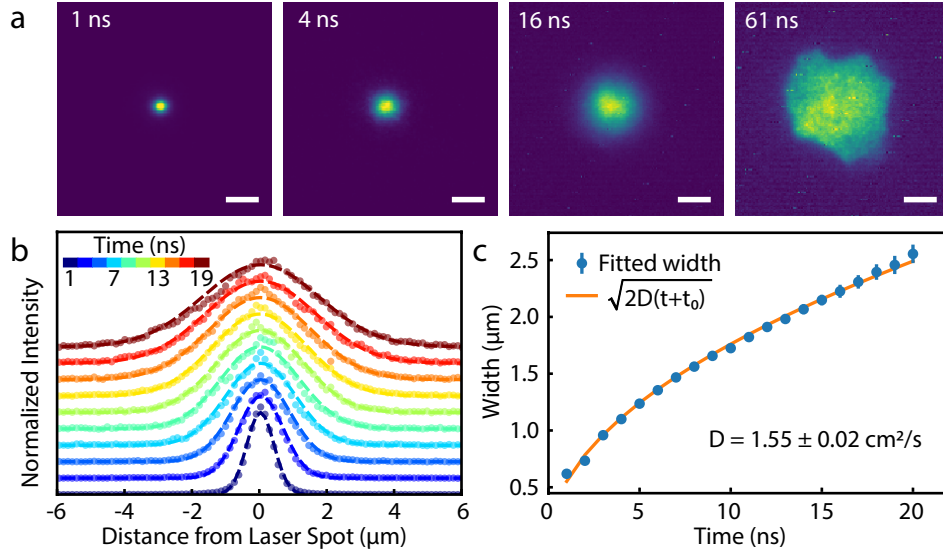


Figure 3.4: **Time-resolved PL imaging measurements of carrier diffusion.** (a) Time resolved PL distribution for 1 ns, 4 ns, 16 ns, and 61 ns time delays after excitation laser pulses. Scale bars are 3 μm . (b) Crosscut of PL distributions and corresponding Gaussian fittings for different time delays. (c) Width of PL distributions fit with a diffusion model, yielding an extracted carrier diffusivity $D = 1.55 \pm 0.02 \text{ cm}^2/\text{s}$.

3.2.3 Carrier Diffusion and Recombination Model

Since the PL intensity $I(x, y, t)$ is proportional to the square of the carrier density $n(x, y, t)$, the PL distribution can be used to infer the dynamics of the carrier density. Note that the exciton binding energy of $\sim 10 \text{ meV}$ is small compared to thermal energy, [50] and we observe no excitonic peak in room-temperature absorption spectra. Thus, we assume that primary carriers are free electrons and holes. Given that the diffusion of electrons and holes is linked by their Coulomb attraction, and since their effective masses are close (approximately 3:4 for FAPbI_3 and 4:5 for similar MAPbI_3 halide perovskite materials [51, 52]), we therefore assume that electron and hole diffusivities are not very different. A 2D Gaussian model that describes carrier distribution is used to fit the square root of the PL distribution to extract the Gaussian carrier width $\sigma(t)$, as shown in Fig. 3.4b. Then the $\sigma(t)$ evolution is used to estimate the carrier diffusivity D through $\sigma(t) = \sqrt{2D(t+t_0)}$ [38], where the parameter t_0 is introduced to account for the initial carrier

distribution ($|t_0| < 0.1$ ns). This diffusion model neglects possible surface diffusion effects, and only holds exactly when linear recombination dominates. Using this, the carrier diffusivity in this grain was found to be 1.55 ± 0.02 cm^2/s .

In order to estimate the systematic error induced by this diffusion model, we numerically simulated a temporal and spatial evolution of carrier distribution according to the phenomenological equation 3.2.

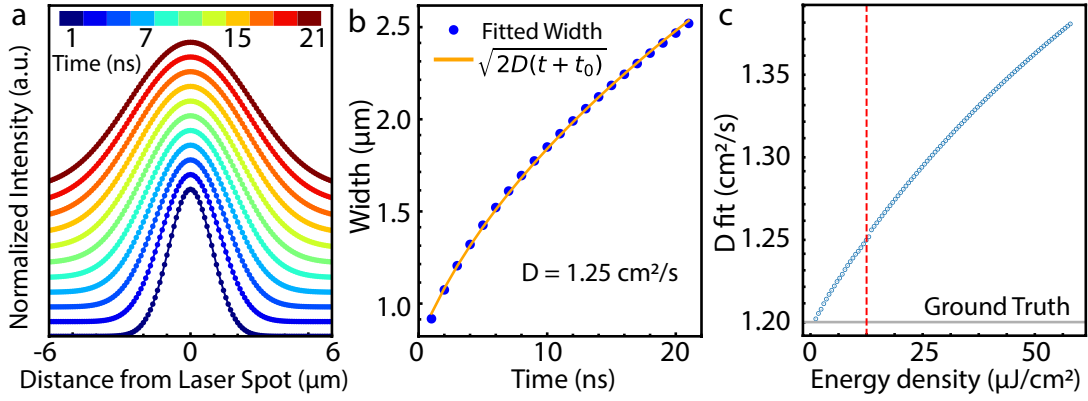


Figure 3.5: (a) Simulated crosscut of PL distribution (solid lines) and corresponding Gaussian fittings (dotted lines) at 1 ns interval time delays with respect to arrival of the laser pulse, for pump energy density 12.5 $\mu\text{J}/\text{cm}^2$. (b) Diffusivities estimated by directly fitting to the simplified diffusion model for the this particular pump energy density. (c) Overestimation of the diffusivity from the ground truth value of 1.20 cm^2/s as pump power increases. Red dashed line shows the pump energy density used in the experiment, gray line shows the ground truth value of diffusivity. The overestimation is under 15% for the entire range of carrier concentrations used in the experiment.

The simulation was done at a range of pulsed energies that includes the values in the experiment, ranging from 1.2 to 60 $\mu\text{J}/\text{cm}^2$, as shown in Fig. 3.5 a,b. The underlying ground truth diffusion coefficient was 1.20 cm^2/s . The numerical solution of the PDE was then fitted with the simplified diffusion model and the resulting values overestimated the ground truth diffusivity as shown in Fig. 3.5 c. The deviations are all within 15% of the ground truth value.

Besides the simulation, we measured experimental diffusivities as a function of pump power as is shown in Fig. 3.6. We tested four different the pump powers, but only observed increase in the measured diffusivity of 6%. Note that this could be due to neglecting second- or higher-order

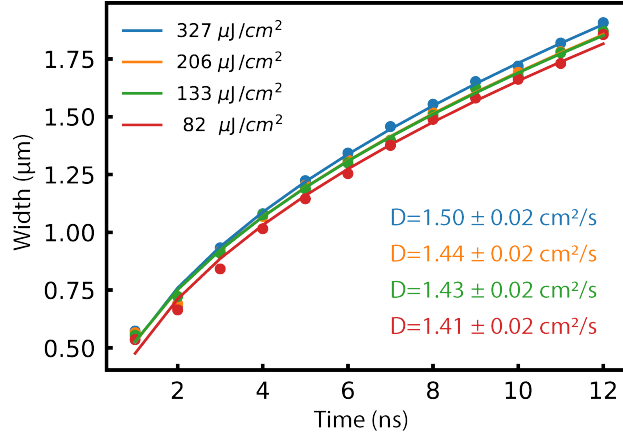


Figure 3.6: Carrier width evolution for different pump powers fitted with the diffusion model.

decay terms when fitting the carrier width evolution as is discussed above. This method thus provides good estimation of the carrier diffusivity in each grains.

3.2.4 Diffusivity Statistics

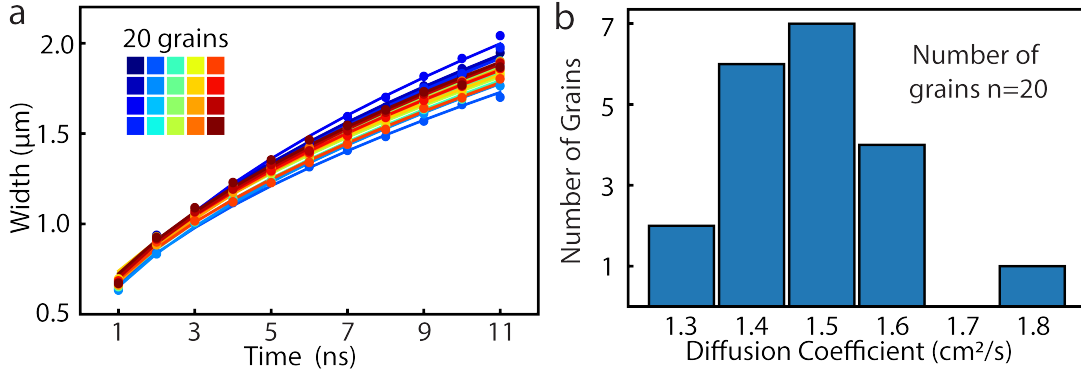


Figure 3.7: **Diffusivity variation in 20 grains.** (a) Width evolution of 20 grains and the corresponding fits to the diffusion model. (b) Histogram of diffusivity D for the 20 grains

The ability of measuring diffusivity D in individual grain is helpful for understanding the variation of carrier transport within FAPbI₃ thin films. Fig. 3.7a shows the corresponding σ evolution for 20 different grains, together with the resulting histogram for diffusivities in Fig. 3.7b. In each grain the PL distribution keeps an approximately symmetric 2D-Gaussian shape while

expanding with time, which indicates that the diffusivity is roughly spatially homogeneous within each grain, even though it varies between $1.3 \text{ cm}^2/\text{s}$ and $1.8 \text{ cm}^2/\text{s}$ in the observed grains.

3.3 Spatial and Temporal PL Spectral Profile

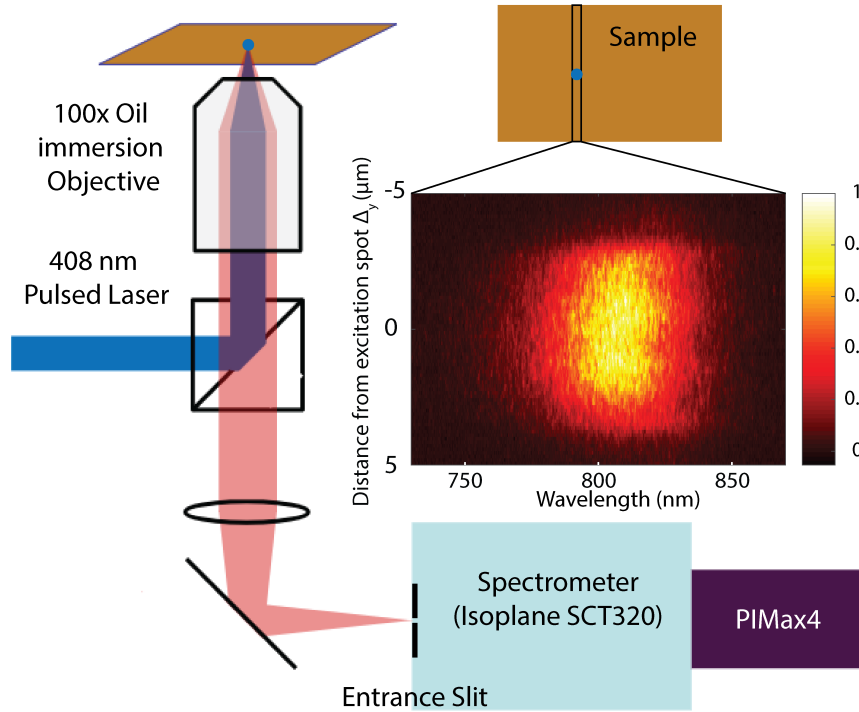


Figure 3.8: Setup for measuring time resolved PL spectral profile.

Besides recording the evolution of carrier distribution, this method can be used to study the spatial dependent PL spectra evolution by combining the fast gated camera with an aberration-corrected Schmidt-Czerny-Turner imaging spectrometer as is shown in Fig. 3.8.

Here, the PL emission was collected from a rectangular window on the sample (300 nm wide, 10 μm tall), and was dispersed by a grating (300 lpm) in the spectrometer to obtain the PL spectra at different time delays. In Fig. 3.9 a, the horizontal axis shows the wavelength information and the vertical axis represents the position y as defined in Fig. 3.8. We observed a slight blue shift for the first nanosecond as compared to the later spectra after which no significant spatial or

temporal dependence was further observed.

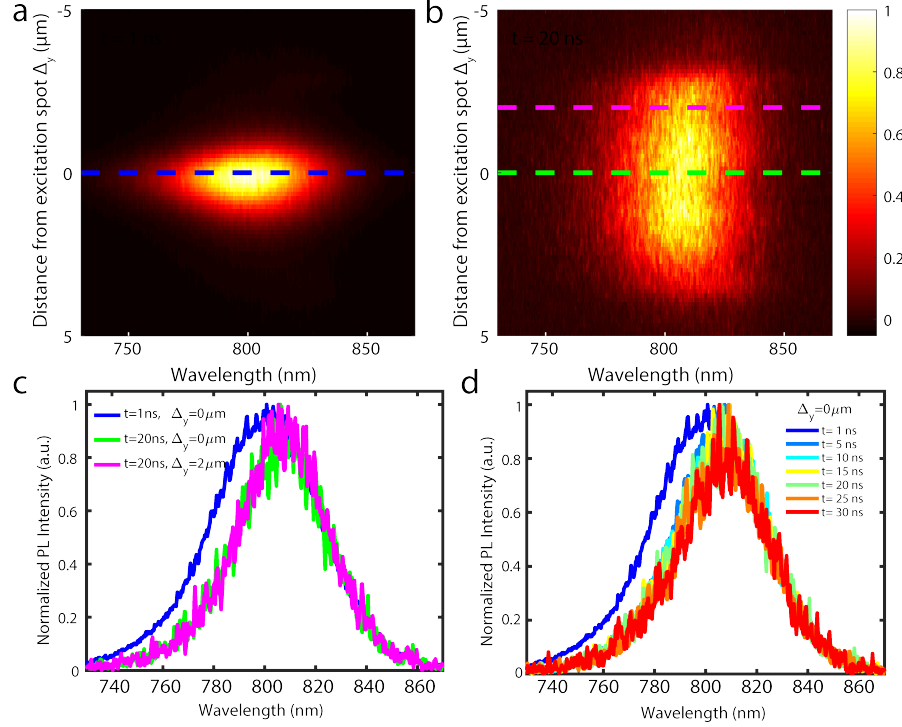


Figure 3.9: Transient spatial PL spectral profile at 1 ns (a) and 20 ns (b). (c) PL spectrum for the excited .(d)

3.4 Carrier Diffusion Under Background Illumination

3.4.1 Carrier Diffusion Accelerated by Background Carriers

Here we also conducted the carrier diffusion measurement under a constant background illumination. Interestingly, carrier diffusion can be accelerated by applying a uniform CW laser illumination to the sample using the configuration shown in Fig. 3.10a, where a homogeneous 401 nm CW laser is applied to the sample together with the focused pulsed-excitation laser at 408 nm. To observe a large change in carrier diffusivity, a relatively high CW laser power density ($150 \text{ W}/\text{cm}^2$) is required. Since constant illumination at this power density could heat and decompose the sample, we modulated the CW illumination to be only turned on intermittently for

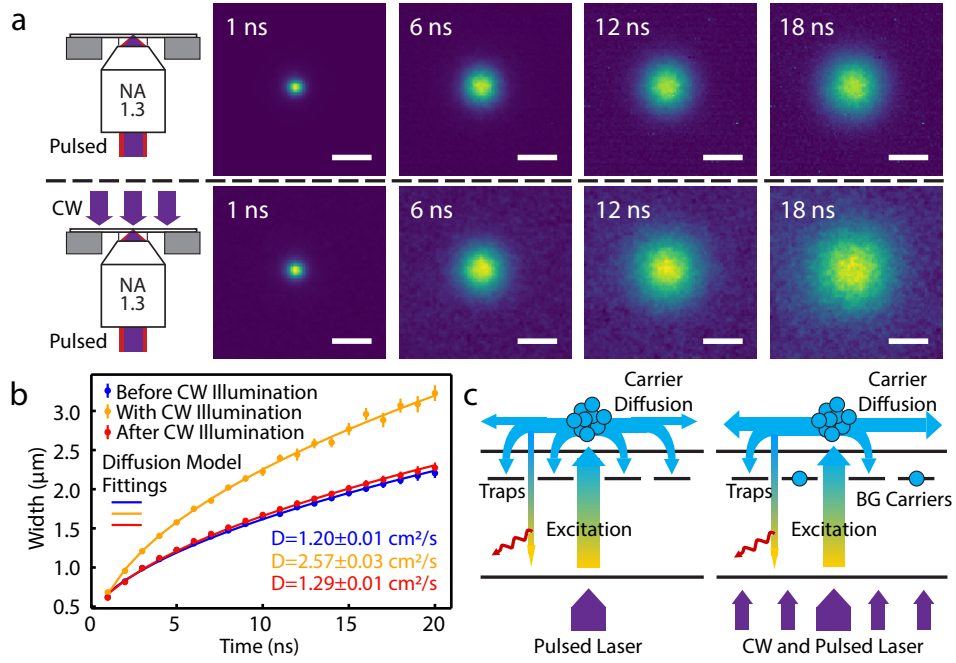


Figure 3.10: **Carrier diffusivity enhancement under quasi-CW uniform laser illumination.** (a) Schematic illustration of CW illumination and transient PL distribution evolution under different illumination conditions. Scale bars are $3 \mu\text{m}$. (b) Width evolution under different illumination conditions and the corresponding diffusion model fits. The transient PL distribution measurements were taken before applying quasi-CW illumination (blue), with the quasi-CW illumination (yellow), and after turning off the quasi-CW illumination (red). The instantaneous CW illumination power density is $150 \text{ W}/\text{cm}^2$, and the average CW illumination power density is $750 \text{ mW}/\text{cm}^2$. (c) Schematic illustrating the increase in carrier mean free path by charge trap screening effect.

500 ns when the PL measurement is running, so that the average CW power is sufficiently low at $\sim 1 \text{ W/cm}^2$ so as not to degrade the sample. For transient photoluminescence (PL) distribution measurements, a 10 kHz repetition rate master clock was used for synchronizing the CW laser, pulsed laser, and camera exposures.

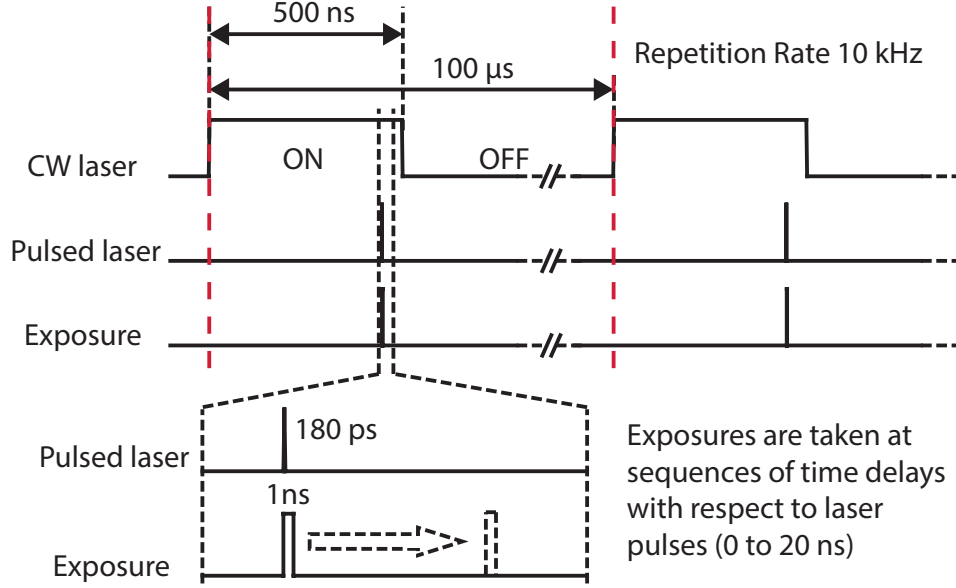


Figure 3.11: Timing Diagram

As shown in Fig 3.11, the CW laser is turned on for 500 ns in each 100 μs cycle (*i.e.* the average power is 0.5% of the instantaneous power), which reduces the heat accumulation in the sample. We refer to this illumination condition as quasi-CW illumination. Using the time-stamp for the turning on of quasi-CW laser as a reference point, laser pulses (180 ps pulse width) arrive at 450 ns, allowing the sample to reach a steady state under the quasi-CW laser illumination. The observation window for transient PL distribution extends from 450 ns to 470 ns. For each transient PL distribution, 1 ns exposure is repeated for 6.4×10^5 cycles at the same time delay to obtain a high signal to noise ratio.

Transient PL images were acquired to measure the diffusivity for the carriers generated from the pulsed laser with and without the homogeneous quasi-CW background laser excitation. In

order to observe the diffusion of carriers generated by the pulsed laser, the PL distribution under quasi-CW illumination alone was measured and subtracted from the transient PL distribution data.

By fitting the width evolution to the simplified diffusion model, we estimate the diffusivity of the grain in Fig. 3.10 to be $1.2 \text{ cm}^2/\text{s}$ before the CW illumination, $2.6 \text{ cm}^2/\text{s}$ under illumination, and returning to $1.3 \text{ cm}^2/\text{s}$ after illumination, as shown in Fig. 3.10b. This shows that the increase in carrier diffusivity induced by the background illumination is reversible.

A possible mechanism for the increase in the diffusivity under background laser illumination is the charge-trap screening effect. In FAPbI_3 thin films, traps can capture carriers and limit their mean free path. However, carriers generated by the quasi-CW illumination can fill and neutralize these traps, preventing them from capturing other carriers. Thus, the mean free path of carriers injected by the pulsed laser may be extended by the background illumination, resulting in a higher diffusivity, as is illustrated by the right panel of Fig. 3.10c.

We also performed the previous measurements under quasi-CW laser power densities from 2 to $400 \text{ W}/\text{cm}^2$. The $400 \text{ W}/\text{cm}^2$ upper bound was chosen because we observed a sharp decrease in PL intensity above $500 \text{ W}/\text{cm}^2$ (averaged power density $2.5 \text{ W}/\text{cm}^2$); this drop could be due to either the increase in sample temperature or heat-related damage. We acquired transient PL images for each power density. Initially, the diffusivity increased with the background laser illumination power, but this effect saturated at a power density of around $250 \text{ W}/\text{cm}^2$, as is shown in Fig. 3.12a. Power-dependent carrier diffusivity measurements were performed on three different grains. Even though the diffusivities for the three grains were different in the dark ($1.52 \pm 0.03 \text{ cm}^2/\text{s}$, $1.42 \pm 0.03 \text{ cm}^2/\text{s}$, and $1.60 \pm 0.03 \text{ cm}^2/\text{s}$ for grain 1, 2, and 3 respectively), their saturation values were roughly the same ($2.87 \pm 0.08 \text{ cm}^2/\text{s}$, $2.89 \pm 0.08 \text{ cm}^2/\text{s}$, and $2.84 \pm 0.08 \text{ cm}^2/\text{s}$).

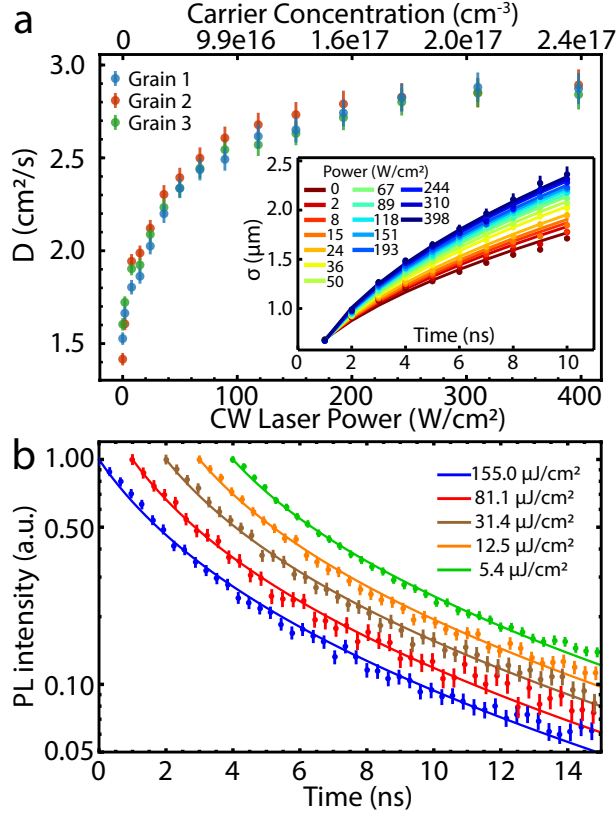


Figure 3.12: **Diffusion and recombination kinetics.** (a) Diffusivities of three grains as a function of CW illumination power. Inset shows the PL width evolution under various CW illumination powers for grain 1. (b) Transient PL decay at different pump powers fit with a recombination and diffusion model. The decay curves are shifted consecutively by 1 ns for clarity.

3.4.2 Background Carrier Density Estimation

In order to estimate the carrier density under a given background CW laser illumination power, it becomes necessary to interpret the experimental data with the full phenomenological relation. [38] A transient PL decay experiment was therefore carried out using different pulsed-laser pump energy densities, and the PL signal was measured using a fast single-photon avalanche diode (PicoQuant, τ -SPAD), which has a higher time resolution of 64 ps.

To model the time dynamics of carrier density $n(x, y, t)$, a phenomenological model consisting of Shockley-Read-Hall recombination, bimolecular recombination, and diffusion terms was considered: [53]

$$\frac{\partial n(r, t)}{\partial t} = G + D\nabla^2 n(r, t) - \frac{1}{\tau}n(r, t) - \beta n(r, t)^2, \quad (3.2)$$

where G corresponds to the carrier generation rate, τ to carrier lifetime, β to bimolecular recombination coefficient and D to the diffusivity. Given that the film thickness is approximately 450 nm (i.e., negligible given the relevant time scale and diffusivity), the diffusion can be modelled as a 2D process.

Due to the Gaussian shape of the pump beam and the observed rotational symmetry of the PL distributions, the initial carrier density was modeled to be a symmetric Gaussian. By assuming that the PL intensity is proportional to n^2 , the numerical solution of this PDE is integrated over the collection area of the optics, and then fit to the normalized time-resolved PL intensity measured by the SPAD.

Given the thinness of the film, diffusion along the surface dominates and the volumetric equation 3.2 turns into Eqn. 3.1, where $n(x, y, t)$ now refers to an areal density of carriers. The coefficient β^* is the area-equivalent to the original volumetric β , the two being related by the thickness of the film d through the relationship $\beta = d \times \beta^*$. Thickness of the film was assumed to be 450 nm.

Furthermore, solutions with radial symmetry can be described by the simplified equation:

$$\frac{\partial n(r, t)}{\partial t} = D \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) n(r, t) - \frac{1}{\tau}n(r, t) - \beta^* n(r, t)^2. \quad (3.3)$$

The equation above was solved numerically using an initial condition with two parameters N_0 and σ ,

$$n(r, 0) = \frac{N_0}{2\pi\sigma^2} e^{-r^2/2\pi\sigma^2}, \quad (3.4)$$

where N_0 corresponds to the total number of carriers at $t = 0$.

The numerical solutions to $n(r, t)$ are related to the normalized time-resolved data $i(t) := \frac{I(t)}{I(0)}$ through

$$I(t) \propto \int_0^R (n(r, t))^2 r \, dr, \quad (3.5)$$

where R is the radius of observation region determined by the optics in the collection path and equal to $3.5 \mu\text{m}$. To avoid complications due to the surrounding grains, the time range was limited to 12 ns. The numerical solution was found on a disk of $10 \mu\text{m}$ in radius, which is large compared to the spreading of the carrier density over 12 ns.

In summary, a particular solution is determined by five parameters D , β^* , τ , σ , and N_0 . A global solution, one that would fit the five experimental curves shown in Fig. 3.12 b, is then determined by a common set of values for D , β^* , τ , and σ , and a set of particular values $N_{0,1}$, $N_{0,2}$, $N_{0,3}$, $N_{0,4}$, and $N_{0,5}$. The solution to this problem was found by minimum χ^2 analysis using the Nelder-Mead non-linear optimization algorithm. Only uncertainties due to shot-noise were considered. The resulting fitted values are shown in the table 3.1.

τ	$(37.2 \pm 0.5) \text{ ns}$
β^*	$(5.3 \pm 0.16) \times 10^{-7} \mu\text{m}^2/\text{ns}$
β	$(2.4 \pm 0.2) \times 10^{-10} \text{ cm}^3/\text{s}$
σ_0	$(0.867 \pm 0.002) \mu\text{m}$
D	$(0.12 \pm 0.01) \mu\text{m}^2/\text{ns}$
$N_{0,1}$	$(8.6 \pm 0.3) \times 10^5$
$N_{0,2}$	$(6.4 \pm 0.4) \times 10^5$
$N_{0,3}$	$(3.6 \pm 0.3) \times 10^5$
$N_{0,4}$	$(2.1 \pm 0.2) \times 10^5$
$N_{0,5}$	$(0.2 \pm 0.1) \times 10^5$

Table 3.1: Resulting values for the global fit of the time-resolved PL experiments.

With the carrier generation rate G calculated from the background illumination power

$$G = \frac{P \times \alpha}{\frac{1240}{\lambda} \times 1.6 \times 10^{-19}} \times 100\%,$$

where P is the power density of the CW laser, α is the absorption coefficient, and λ is the wavelength of the CW laser. The steady-state carrier concentration can be estimated using Eq. 3.6.

$$G - n/\tau - \beta n^2 = 0, \quad (3.6)$$

The corresponding carrier concentration for a background illumination power of $250 \text{ W}/\text{cm}^2$ (at which the diffusivities saturate) is $(1.8 \pm 0.3) \times 10^{17} \text{ cm}^{-3}$.

3.4.3 Trap Screening Effect by Background Carriers

The measured diffusivity improvement under CW illumination reflects an increase in carrier mean free path, which could result from trap screening by the background carriers. This hypothesis is also consistent with the saturation observed in the power-dependent diffusion measurements shown in Fig. 3.12a. Initially, carrier diffusivity increases with CW laser power as more traps are filled by background carriers; this is a trap-limited regime in which the trap-carrier interactions impede transport. Once the illumination power density reaches $\sim 250 \text{ W/cm}^2$, carrier diffusivity plateaus as traps become saturated. The trap occupation dynamics can be determined if the trap densities and energy levels are known [53, 54]. While the actual trap densities in our samples require further study, our results point to the same order of magnitude as the saturation background carrier concentration (10^{17} cm^{-3}), consistent with previous reports on surface trap density for similar methylammonium lead triiodide (MAPbI_3) perovskite material [55]. As shown in Fig. 3.12a, the diffusivity saturation level for multiple grains is quite similar, which suggests that these grains have a similar intrinsic diffusivity and that the difference in their measured diffusivity values in the dark is due to different trap densities. Interestingly, our results suggest that carrier diffusion is still in the trap-limited regime under one-sun illumination ($\sim 100 \text{ mW/cm}^2$).

In conclusion, we have presented a wide-field transient PL imaging method to measure carrier diffusivity in perovskite thin films. In contrast to point detectors used in conventional transient PL spectroscopy setups, the fast-gated intensified camera sacrifices picosecond time resolution for the ability to measure in parallel a wide field of view. In the context of carrier transport studies in organic-inorganic halide perovskites, one-nanosecond time resolution is sufficient for resolving carrier transport, whereas spatial information over length scales comparable to grain size is important for accurately estimating carrier diffusivity. Using our method, carrier diffusivity changes were studied as a function of background carrier density created by CW illumination, and discussed within the context of trap-carrier interactions. We show that even in the absence of

grain and sub-grain boundary scattering, the carrier diffusion in FAPbI₃ is still in the trap-limited domain under one-sun illumination. Such carrier-trap interactions would limit carrier extraction and ultimately limit the short circuit current and quantum efficiency of solar cell devices.

Chapter 4

Photoluminescence Microscopy for Identifying Sub-grain Boundaries in FAPbI₃ Thin Films

4.1 Introduction

It is important to characterize the grain boundaries in perovskite materials, because grain boundaries can reduce power conversion efficiency (PCE) by limiting carrier diffusion and introducing nonradiative recombination sites. Due to the formation of grain-boundary grooves during OIHP film growth [56], many techniques for identifying grain boundaries rely on surface morphology characterization, for example, using atomic force microscopy (AFM) or scanning electron microscopy (SEM) [57]. However, not all boundaries exhibit clear surface features.

In this chapter, we first intrude the type of boundaries in crystalline materials and the electron backscatter diffraction method for characterizing the crystal orientations. After that, we show experimental evidence for the existence of special sub-grain boundaries in formamidinium lead

iodide (FAPbI_3) perovskite thin films. These boundaries that we identified using PL microscopy cannot be observed by either AFM or SEM. However, they present significant barriers for carrier transport.

4.1.1 Crystal Boundaries

In a single composition crystalline material, boundaries are the regions or interfaces that separate two parts that have different crystal orientations. In general, grain boundaries can be categorized into high-angle boundaries and low-angle (or sub-grain) boundaries based on the crystal orientation difference across them. Schematic of the boundary categories is shown in Fig. 4.1. In low-angle boundaries, the misorientation between the two regions results in a plane of dislocations along the boundary. Twin boundaries are a special category of boundaries where the two regions across the boundary have crystal orientations related by mirror reflection. Twin boundaries can be generated by deformation or associated with high-to-low symmetry polymorph crystal structure transitions such as tetragonal to monoclinic. Using optical or SEM micrographs, two features can be observed about twin boundaries: they are usually straight, and they often occur parallel to other twin boundaries. [58]

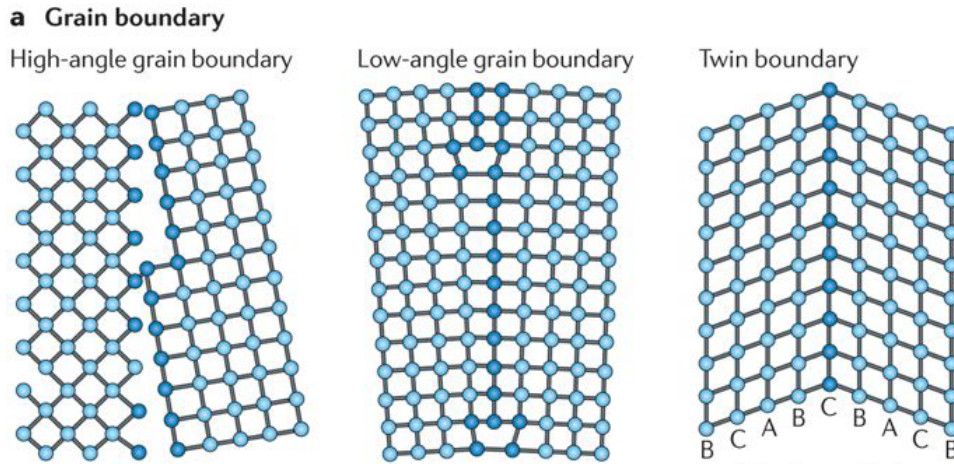


Figure 4.1: Schematic of high-angle boundary, low angle boundary and twin boundary. Figure adapted from publication by Lu et al. [7].

4.1.2 FAPbI₃ Kikuchi Pattern

Kikuchi patterns can be calculated given the atomic positions within a unit cell and the crystal structure of the material. FAPbI₃ has been reported to have a cubic perovskite unit cell of dimension $\sim 6.36 \text{ \AA}$. [1] The atomic positions of FAPbI₃ is adapted from reference by Weller *et al.* and used for simulating its Kikuchi pattern are listed in table 4.1.

Atom	X	Y	Z
C	0.50	0.52	0.5
N	0.68	0.43	0.5
N	0.32	0.43	0.5
H	0.50	0.67	0.5
H	0.81	0.52	0.5
H	0.70	0.26	0.5
H	0.19	0.52	0.5
H	0.30	0.26	0.5
Pb	1	0.97	1
I	0.50	0.97	1
I	0	0.46	1
I	0	0.92	0.5

Table 4.1: Atomic positions in the unit cell of FAPbI₃ for Kikuchi pattern simulation as is reported in reference [1]

The Kikuchi pattern for FAPbI₃ was simulated using the above atomic position data from Weller using *Twist*, a piece of software produced by the company *Oxford Instruments*. The corresponding Kossel cones are shown in Fig. 4.2b. The Kikuchi pattern was used for determining the crystal orientation of each grain in a polycrystalline FAPbI₃ thin film.

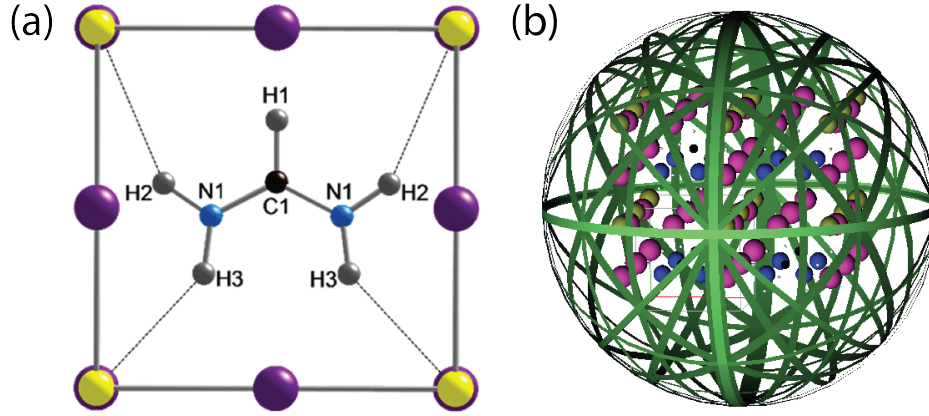


Figure 4.2: (a) Unit cell structure of α -phase FAPbI₃. NH-I hydrogen bonds are shown as dashed lines. Figure adapted from Reference [1]. (b) Simulated Kossel cones for FAPbI₃.

4.2 Sub-grain Boundary Revealed by Photoluminescence Microscopy

4.2.1 Photoluminescence Microscopy for Characterizing Carrier Transport

To study the carrier transport barriers in large grain FAPbI₃ thin films, a photoluminescence (PL) imaging method is established, and the PL intensity is used as an indication for the local carrier density.

Thin film samples of polycrystalline FAPbI₃ (thickness ~ 500 nm) were excited by a focused 532 nm laser (Verdi, Coherent) with a 100X Nikon oil immersion objective (spot size around 250 nm, average power density around 320 mW/cm²) in an inverted microscope system (TE2000, Nikon). PL signal was collected by the same objective and imaged with a CCD camera (Pixis 1024B, Princeton Instruments). The PL spectrum of the sample has a peak centered at 810 nm with a 40 nm full-width at half-maximum (FWHM). It was observed that the PL emission area was much larger than the laser pump size. PL from a given region in the film can have one of

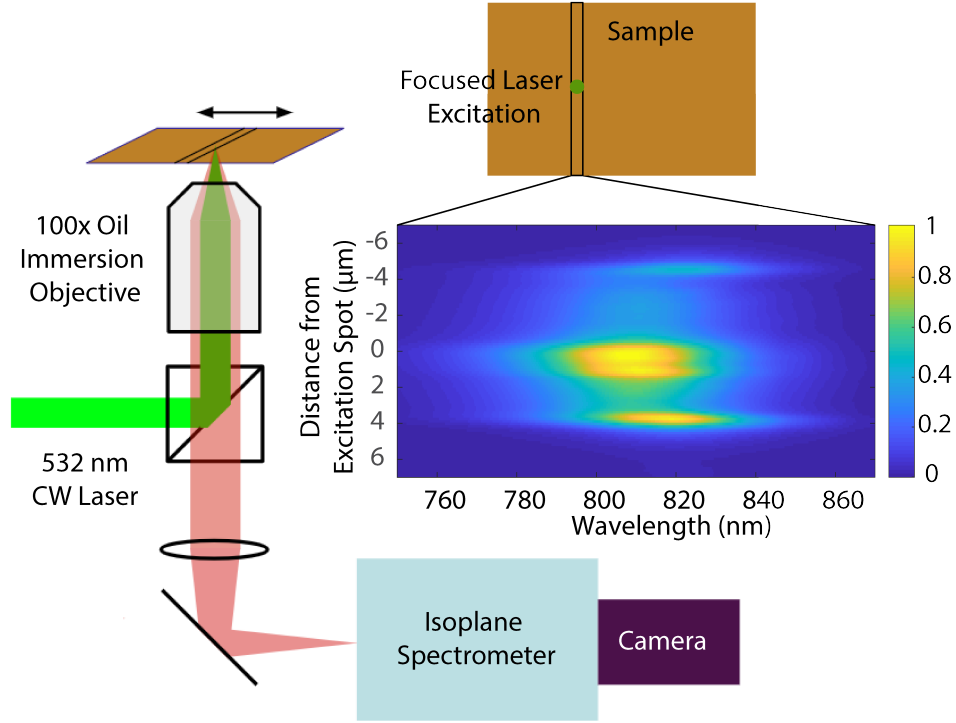


Figure 4.3: Schematic of push-broom scan setup.

two different sources: (1) PL directly produced by recombination in that region (local PL), and (2) PL produced elsewhere (by recombination) but which was guided by total internal reflection across the film and scattered out in the given region (scattered PL)

To ensure that the PL that is actually indicative of carrier density at a given region in the sample, it is desirable to filter the scattered PL. Fortunately, the spectrum of the scattered PL is red-shifted by absorption as it travels through the film. To quantify the amount of red-shift in the scattered PL, a “push-broom” scan was performed to compare the PL spectra at the excited spot (where most PL would be local) with the spectra further away from the excitation spot (where the relevance of scattered PL would increasingly grow). In the push-broom scan (see Fig. 4.3), spatial and spectral information are collected at the same time. To accomplish this the sample is placed on a nano positioning stage (MCL LP100) and a focused 532 nm laser is used for excitation. By closing down the entrance slit on an imaging spectrometer (IsoPlane),

PL is collected at each stage of the scan from a 300 nm wide, 10 μm tall rectangular region. The spectrometer disperses the collected PL which is then collected by a CCD, the result being the spectra as a function of position across the height of the rectangular observation region. After this is done, the sample is moved 300 nm in the direction of the short edge of the rectangular collection region, and spectra are again collected. This process is repeated to collect information from the whole sample.

With the push-broom scan data, PL distribution images at certain wavelength range can be reconstructed. Figure 4.4 (b) shows the PL distribution of one grain at the full wavelength range, wavelength greater than 800 nm range and less than 800 nm range. Here, grain boundaries serve as scattering centers and are associated with more scattered PL (marked with a cross in Figure 4.4 (b)). As a result, it appears brighter than the inside of the grain. It is found that the effect scattered PL can be reduced by only looking at wavelengths range below than 800 nm, and a 800 nm short pass filter is thus used in the subsequent PL distribution imaging experiment.

4.2.2 Surface Morphology of Sub-grain Boundary

To study the carrier transport properties across the boundaries in FAPbI₃ thin film, the PL distribution and the surface morphology images corresponding to the same region on sample are acquired and compared.

Figure 4.5(a-c) shows representative optical, scanning electron microscope (SEM), and atomic force microscopy (AFM) images of a large-grained FAPbI₃ perovskite thin film produced by low-temperature solvent-vapor annealing [49].

The optical micrograph shown in Figs. 4.5a was recorded in transmission mode under Köhler illumination with a halogen white-light source using the same inverted microscope and camera setup described above for the PL measurements (TE2000, Nikon; Pixis 1024B, Princeton Instruments). The SEM image shown in panel Figs. 4.5b was obtained using a field-emission SEM (Zeiss, LEO 1530 VP) at an acceleration voltage of 5 kV. The atomic force microscopy

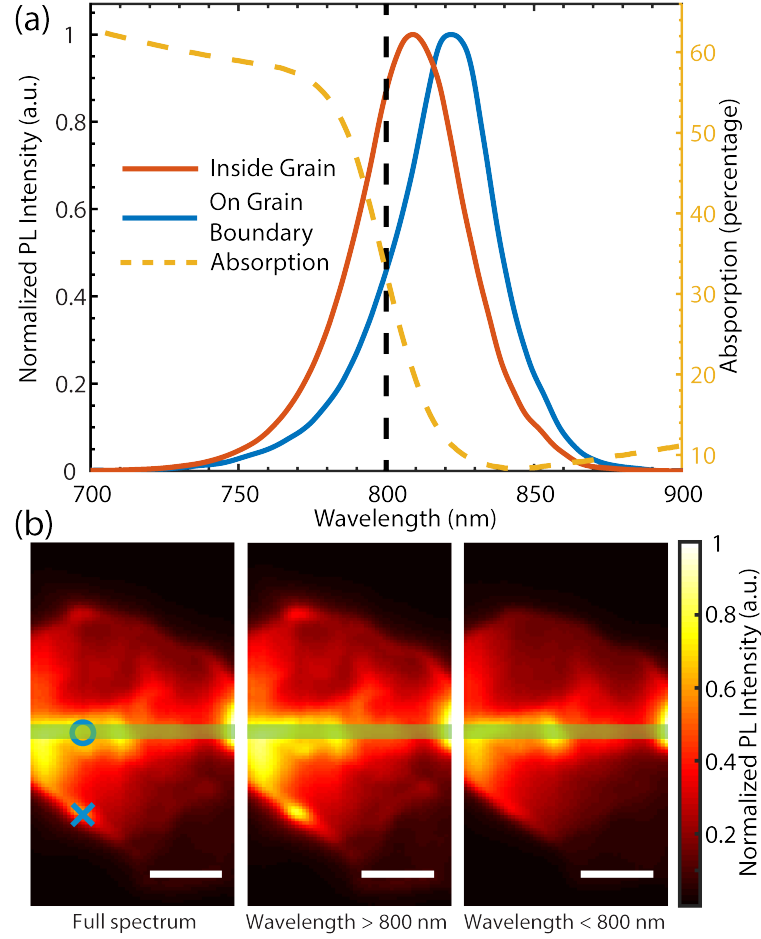


Figure 4.4: (a) Absorption spectrum, and normalized PL spectra for regions inside the grain (marked in (b) by a circle) and on a grain boundary (marked in (b) with a cross). The black dashed line corresponds to wavelength of 800 nm. (b) PL distribution images for different wavelength ranges reconstructed from the push-broom scan. All scale bars are $2\ \mu\text{m}$. Green line corresponds to the excitation spots.

(AFM) measurements were obtained in contact mode (MFP3D Origin, Asylum Research with ASYELEC.01R2 probe tips, Asylum Research). Based on the visible grain-boundary grooves, one might assume that the central (“penguin”-shaped) feature is a single grain. To study this feature, we examine the spatially-resolved PL intensity distribution for focused laser excitation.

Superimposed onto the SEM image, Figure 4.6(a-c) shows the resulting PL images for excitation by a near-diffraction-limited $\sim 250\text{-nm}$ spot located in the top and bottom regions, respectively. Note that the luminescent areas are much larger than the excitation spot, because

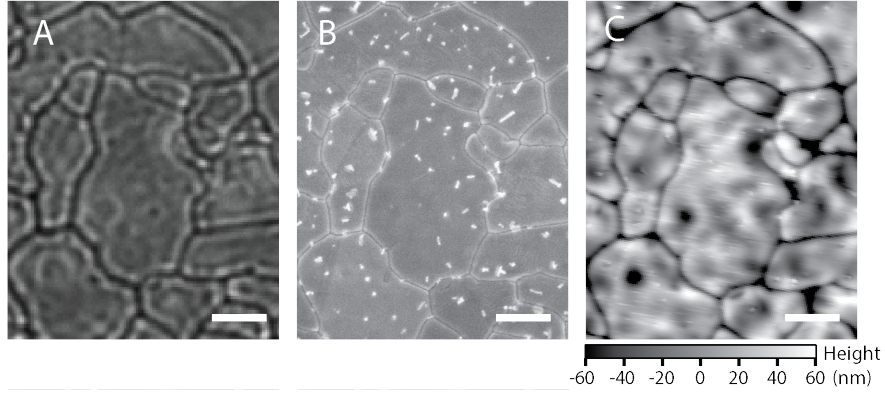


Figure 4.5: Surface images of FAPbI₃ perovskite thin film obtained by (a) optical microscopy, (b) SEM, and (c) AFM measurements.

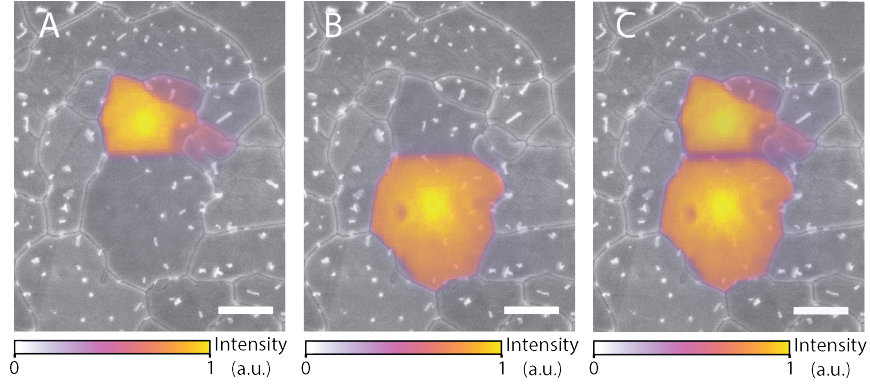


Figure 4.6: (a-c) Focused excitation PL intensity distributions superimposed onto the SEM image.

carriers are diffusing prior to recombination. Both PL images show a sharp straight discontinuity that bisects the feature and clearly prevents carrier diffusion, consistent with prior work showing reduced carrier transport across visible grain-boundary grooves [59, 60]. However, in this case, there is no visible surface feature at this sharp discontinuity. Using the relative PL intensity drop as a qualitative indicator for carrier diffusion, it is interesting to note that carriers in Fig. 4.6(a) appear to diffuse more readily across the visible grain-boundary grooves on the right hand side than they do across the invisible sub-grain discontinuity. Superimposing the PL images for excitation in the top and bottom regions, as shown in Figure 4.6(c), the straight line that divides them has a reduced PL intensity.

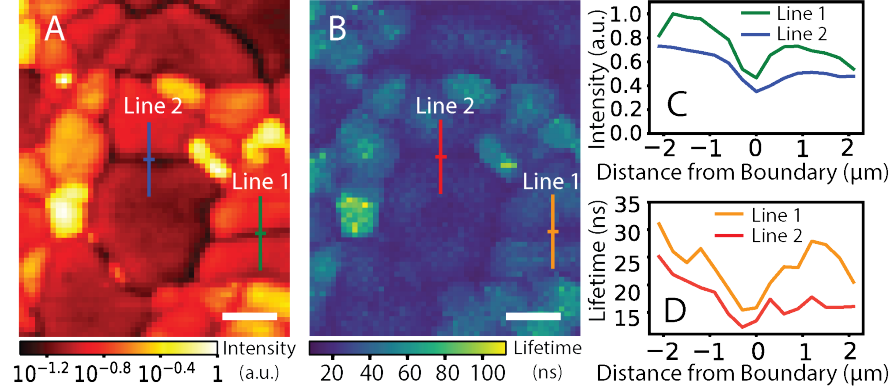


Figure 4.7: (a) PL intensity and (b) PL lifetime maps. All scale bars are $3 \mu\text{m}$. (c-d) Averaged PL intensity and lifetime comparison between boundaries with (Line 1) and without (Line 2) visible grooves.

To study carrier recombination, we use scanning confocal microscopy to record time-resolved PL emission as a function of excitation position across the sample. The time-resolved PL data was first normalized so that $I(0) = 1$ and then fitted with a bi-exponential decay model $I(t) = I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2}$. The least squares method was used for fitting the model with uncertainties obtained from background and shot noises added in quadrature $\sqrt{N_{\text{shot}}^2 + N_{\text{bg}}^2}$. Figure 4.8 shows an example of such fitting. The average lifetime used in Fig. 4.7b,d is a weighted average of τ_1 and τ_2 . The weights being proportional to the total photons of the two decays: $w_i = \int_0^\infty I_i e^{-t/\tau_i} dt = I_i \tau_i$.

Figure 4.7(a-b) demonstrates that the boundary cutting the grain in half is associated with a reduced PL intensity and shortened carrier lifetime, both of them comparable to that observed at nearby grain-boundary grooves [see Fig. 4.7(c-d)]. These results show that this carrier transport boundary, which is invisible to AFM or SEM characterization, is associated with significant nonradiative recombination.

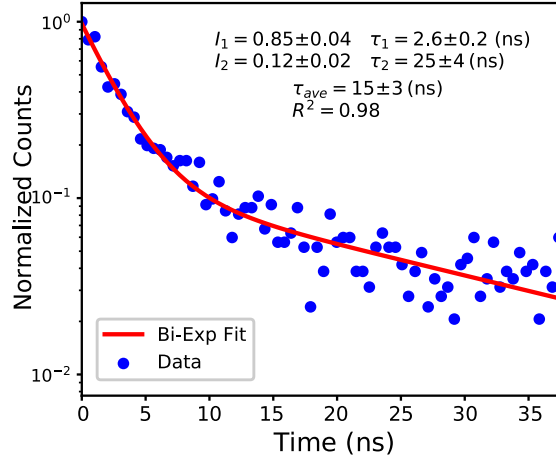


Figure 4.8: Time-resolved PL intensity and bi-exponential decay fit.

4.3 Crystal Orientations Across Sub-grain Boundaries

We readily observed similar carrier transport boundaries in all large-grained FAPbI_3 perovskite thin film samples that we measured. Figure 4.9 shows several more examples. In contrast to normal grain boundaries, these boundaries are straight and groove-less. While these boundaries often bisect the grain into two regions, Fig. 4.9(d) highlights an example where an apparent grain is segmented into five regions by four such boundaries.

4.3.1 Electron Backscatter Diffraction

Note that the SEM image was taken at a tilted angle of 70° for purposes of the EBSD measurement. The raw SEM image is shown in Fig. 4.10a. Figure 4.10b shows the image corrected for perspective using the corresponding optical reference image shown in Fig. 4.10c. The parallel nature of the sharp discontinuities in Fig. 4.9(d) suggests that they are special boundaries, reminiscent of twin boundaries found in other perovskite materials. [8]

To study the relative crystal orientations of the sub-grain regions, we acquired spatially resolved electron backscatter diffraction (EBSD) Kikuchi patterns across the sample, and then

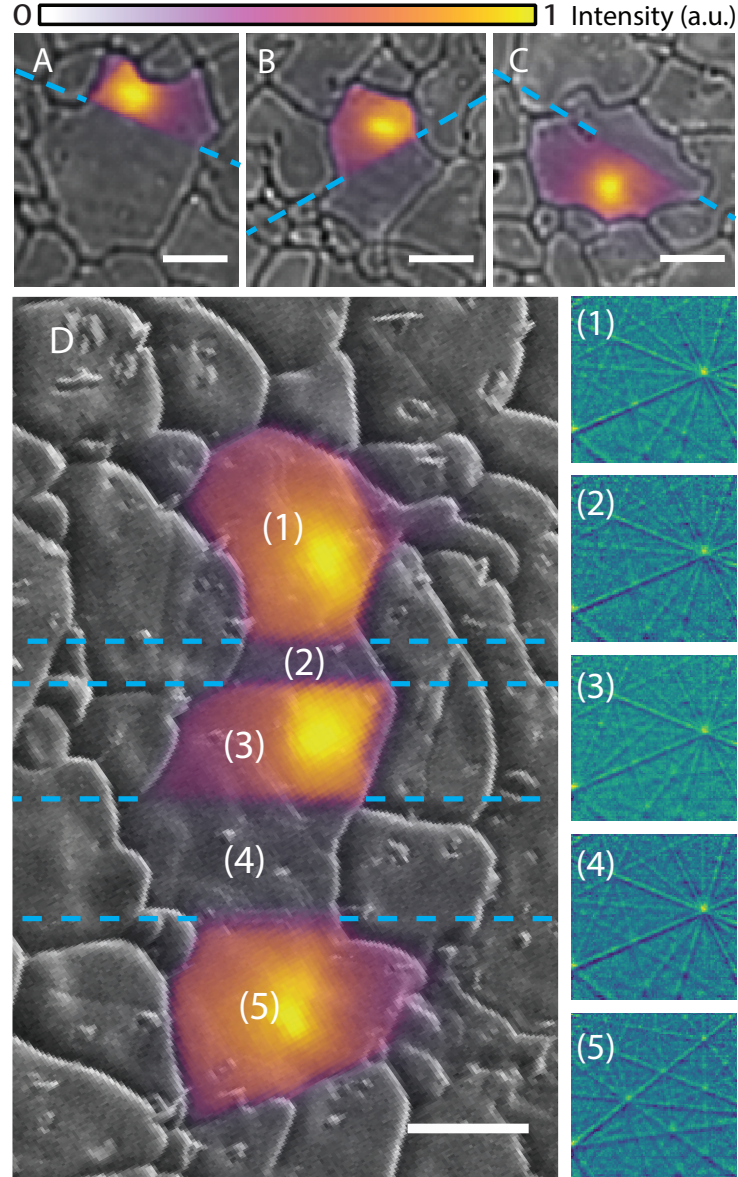


Figure 4.9: PL intensity distribution images for four different apparent grains superimposed onto optical microscopy images (a-c) and SEM image (d). Dashed blue lines highlight the special boundaries, and all scale bars are $3\ \mu\text{m}$. Right panels in (d) show EBSD Kikuchi patterns from regions labeled 1-5.

averaged these patterns for each of the five labeled regions in Fig. 4.9. Due to the varying sizes of the subgrain regions, the number of patterns used for the averages for regions 1 through 5 were 40, 17, 43, 40, and 67, respectively. The EBSD detector used was model *Symmetry* from Oxford Instruments. The parameters used during data acquisition were a 30 kV acceleration voltage and

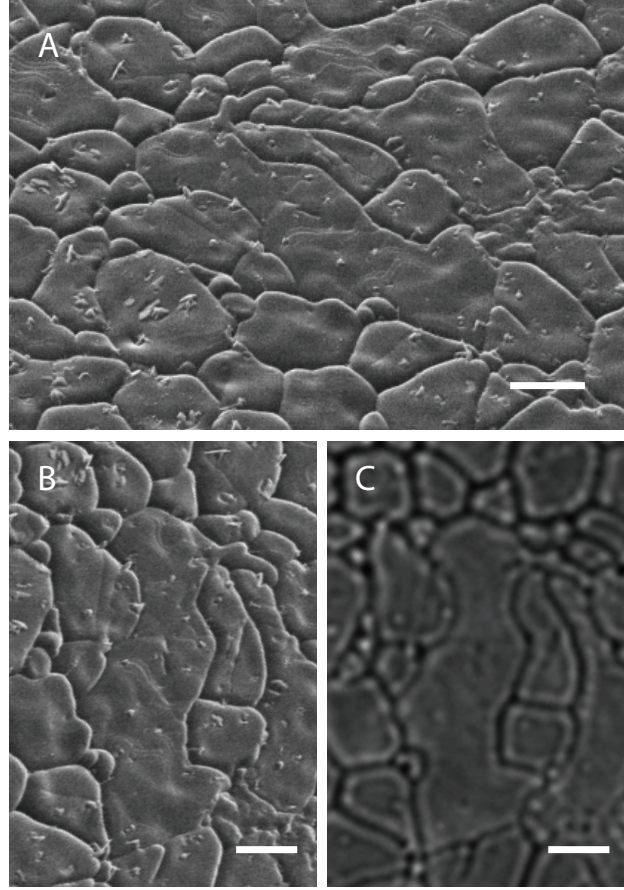


Figure 4.10: (a) Raw SEM image. (b) Rotated and scale-corrected SEM image. (c) Optical microscopy image. All scale bars are $3\ \mu\text{m}$.

a $0.34\ \text{nA}$ beam current.

While the average EBSD pattern for region 5 is unique, regions 1-4 exhibit identical Kikuchi patterns. This suggests that their crystallographic orientation is closely related (either identical or rotated by a symmetry angle). While further characterization will be necessary to determine their precise crystallographic nature, it is clear from the EBSD and PL data that these special boundaries are coherent, akin to twin boundaries. The crystal orientation can be determined by fitting the Kikuchi patterns for the five regions as is shown in Fig. 4.11. The Euler angles for the crystal orientations of regions 1-4 and region 5 are $(16.5^\circ, 84.5^\circ, 52.2^\circ)$ and $(5.9^\circ, 86.6^\circ, 21.1^\circ)$.

Besides the straight subgrain boundaries shown above, subgrain boundaries with a turning point can also be found in the large-grained FAPbI_3 perovskite thin film samples, as is shown

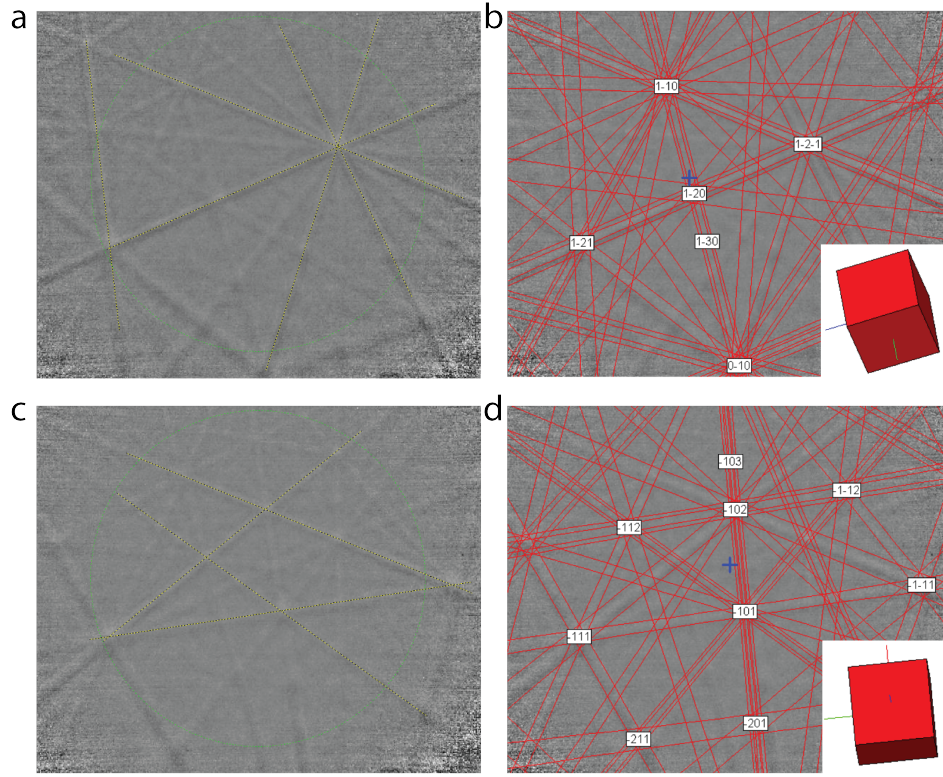


Figure 4.11: Kikuchi pattern fitting for (a) region 1-4 and (b) region 5. The label are the Miller index for a plane.

in Fig 4.12(a,b). When more than one subgrain boundaries exist in a single grain, they can also intersect rather than being parallel with each other (Figure 4.12(c)). The angles between two straight intersecting subgrain are in range of 50 to 60 degrees.

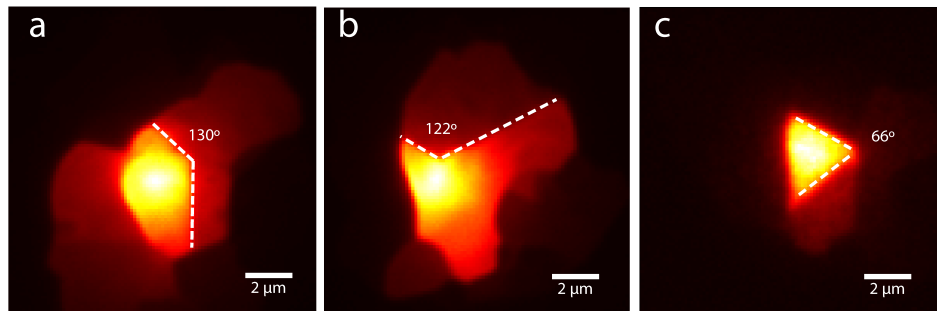


Figure 4.12: (a-b) Subgrain boundaries with turning points. (c) Two subgrain boundaries intersect.

4.4 Conclusion

As evidenced by the PL data, the significant impact of these special boundaries on carrier transport may help explain why PSCs device performance has not scaled with apparent grain size. [61, 62] While further investigation is required to quantify the prevalence and impact of special boundaries for other OIHP materials, the results presented in this chapter show that PL microscopy can provide a powerful (rapid and non-destructive) means of revealing these otherwise invisible boundaries and characterizing their effects on carrier transport for large-grained OIHP films.

Chapter 5

Charge Carrier Transport in Ferroelastic Twin Boundaries in MAPbI₃ Single Crystals

5.1 Introduction

It is well known that grain boundaries in perovskite materials can reduce the solar cell power conversion efficiency by limiting carrier transport and providing nonradiative recombination sites. In the previous chapter, we showed that sub-grain boundaries in FAPbI₃ have a similar impact. There exists another special type of boundaries in MAPbI₃ single crystal called ferroelastic twin boundaries (FTBs), whose impact on the carrier transport and recombination remains unexplored. Solar cells and photodetectors fabricated with these single crystals already show a high PCE of 21% [63] and an excellent sensitivity with a light detection limit as good as 0.35 pW/cm² [64].

In this chapter, we first give an introduction to FTBs in MAPbI₃, and then present a polarized

light microscopy method for observing them. Subsequently we study the behavior of carrier transport across the FTBs using a PL imaging method. We confirm the benign nature of the FTBs using scanning confocal microscopy. In contrast to regular grain boundaries, FTBs have little effect on carrier transport and are not associated with non-radiative recombination sites.

5.1.1 Twin Boundaries in MAPbI₃

The formation of TBs in OIHPs films can be driven by strain in the lattice induced by mismatch in thermal expansion coefficients or the crystal phase transitions during the annealing process. Domain-like structures in MAPbI₃ thin films were first discovered by Hermes *et al.* using piezoresponse force microscopy (PFM). [65] Based on the behaviour of the TBs under stress, Strelcove *et al.* determined that the nature of the domains is ferroelastic and not ferroelectric, this both in MAPbI₃ thin films and single crystals. [9]. Meanwhile, using low-dose transmission electron microscopy (TEM) and selected area electron diffraction (SAED), Rothmann *et al.* directly observed the structure of these ferroelastic twin-domains (FTDs), and identified that they are formed as a result of the cubic-to-tetrahedral phase transition of MAPbI₃. [8]

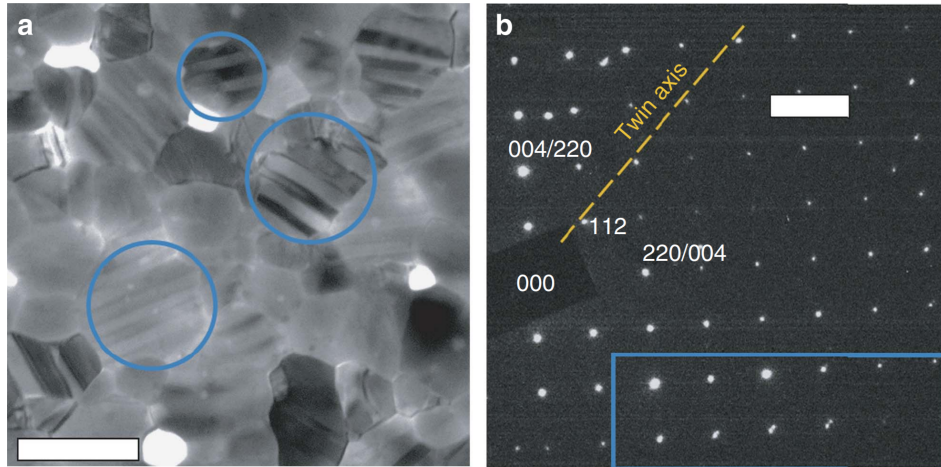


Figure 5.1: a. Bright-field TEM image of a pristine MAPbI₃ thin film. A stripe contrast is visible through some of the grains. Scale bar is 500 nm. b. Diffraction pattern taken from a grain exhibiting stripe contrast showing two single-crystal patterns with a mirrored relationship. Figure adapted from reference [8]

5.1.2 Polarized Optical Microscopy for Observing Twin domains in MAPbI_3

Polarized optical microscopy uses linearly polarized illumination rather than randomly polarized light as is used in conventional light microscopy. It is widely used to identify and characterize optically anisotropic samples such as birefringent materials, where image contrast is much improved since polarized light interacts strongly with anisotropic materials. A polarized light microscope can be constructed by adding two polarizers in a conventional optical microscope. One polarizer is placed between the illumination source and the sample to ensure the incident light is polarized, and the other polarizer is usually rotatable and located on the collection path (between sample and eye-piece/camera). Usually the polarization axis of the two polarizers are set to be perpendicular to maximize the image contrast.

MAPbI_3 single crystals are anisotropic and their refractive index depends on the crystal orientations. The transmission or reflection of the incident polarized light depends on the relative orientation between the polarization of incident beam and the principal optical axes of the MAPbI_3 crystal. A polarized light microscopy image of FTDs in a MAPbI_3 single crystal sample is shown in Fig. 5.2.

The domain boundary types and the possible angles between them are determined by the crystal symmetry. When the MAPbI_3 cools down after the thermal annealing process, a phase transition from cubic to tetrahedral occurs at 327 K, which can produce six types of domain orientations as is shown in Fig. 5.3. The domain walls can have angles of 0° , 90° , or 45° in the principal planes of the crystal ((001), (100), and (010)), and they may form 70° and 110° angles in other planes such as the (110) planes. [9]

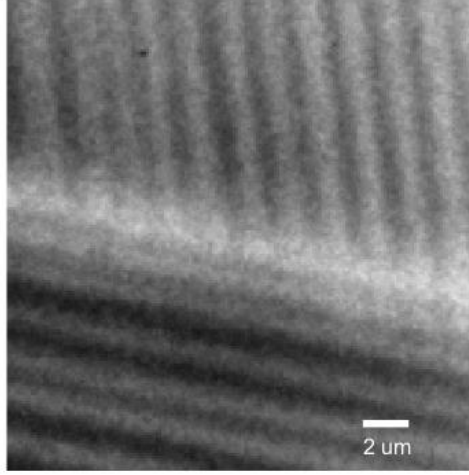


Figure 5.2: Polarized light microscopy image of MAPbI₃ single crystal. The bright and dark regions correspond to different ferroelastic domains in the MAPbI₃ single crystal sample.

5.2 Sample Preparation and Characterization

5.2.1 Sample Preparation

Here, we used MAPbI₃ single crystals with FTBs and multi-crystalline films with GBs as a control to study the impact of FTBs on carrier transport. Using photoluminescence (PL) imaging techniques, FTBs were revealed to affect neither carrier transport across them, nor carrier recombination.

This project was a collaboration with Xun Xiao, Dr. Yanjun Fang and Prof. Jinsong Huang from the University of North Carolina at Chapel Hill, who also provided the samples, characterized FTBs with scanning probe microscopy, and collaborated on experimental design and data analysis. The MHP single crystals were grown on glass substrates by a recently developed space-confined lateral crystal growth method, [63, 64] which produces thin single crystals with typical lateral sizes of 0.5 - 5 mm and the thicknesses of 10 - 50 μm . The ferroelastic twin domains in the as-grown MAPbI₃ single crystals can be clearly resolved through polarized optical microscopy

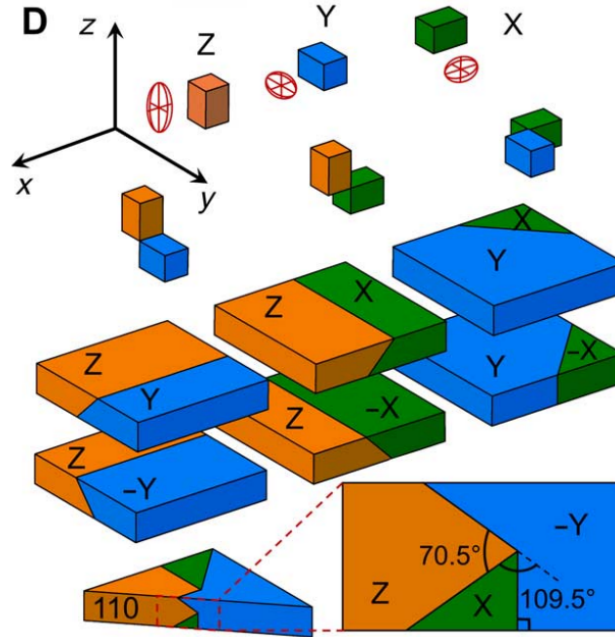


Figure 5.3: Permissible domains of the MAPbI_3 tetrahedral phase. At the cubic-to-tetrahedral transition, the tetrahedral unit cell can form with the c axis aligned along any of the three axes (x , y , and z) of the parental cubic phase, leading to three possible configurations (X , Y , and Z). The six possible domain orientations that are characterized by domain walls intercepting at 0° , 90° , or 45° in the principal planes of the parental phase and at 70° and $\approx 110^\circ$ in the (110) plane. Figure adapted from reference [9].

and the ferroelastic nature of these domains is confirmed by strain induced domain wall motion.

5.2.2 Photoluminescence Imaging Method for Monitoring Carrier Transport

The impact of the ferroelastic twin boundaries on carrier transport across them was investigated with a PL imaging method. In this method, a 532 nm CW laser was focused (near-diffraction limited 250nm spot) on the sample to generate charge carriers. The photoexcited electrons and holes diffuse in all directions in the sample, driven by carrier concentration gradients. During the diffusion process, radiative recombination of excess electrons and holes generates PL, and the PL intensity reflects the carrier concentration at the location. Since PL emission needs the presence

of both excess electrons and holes, the PL images would show a discontinuity at the boundary if either electrons or holes were blocked by the boundary.

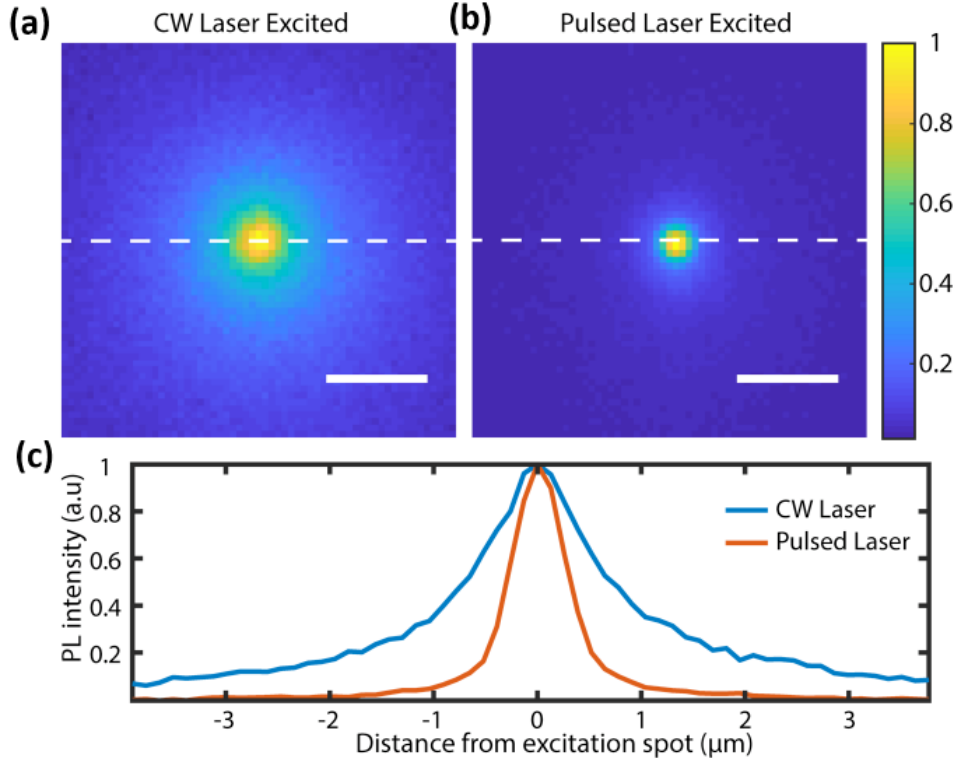


Figure 5.4: (a) PL imaging under CW laser excitation; (b) PL imaging under pulsed laser excitation ($120 \mu\text{J}/\text{cm}^2$); (c) PL intensity distribution cross-cut along the white dashed line shown in (a) & (b). Scale bars are $2 \mu\text{m}$

As discussed in Chapter 4, it becomes necessary in this type of method to determine the relative importance of local PL and scattered PL. To find out the degree to which the PL intensity distribution is caused by scattered PL within the crystal, concentration dependent PL measurements were performed. In theory, the spreading of PL should be independent of carrier concentration if it were caused by scattered PL. However, as shown in Fig. 5.4 the PL distribution is much narrower under high carrier concentration. This is due to a decrease of effective carrier diffusion length when fast recombination pathways (*e.g.* bimolecular and Auger recombination) become dominant at high carrier concentration. To rule out the effects of surface roughness and make a clear connection between the PL distributions and carrier density, we chose samples with

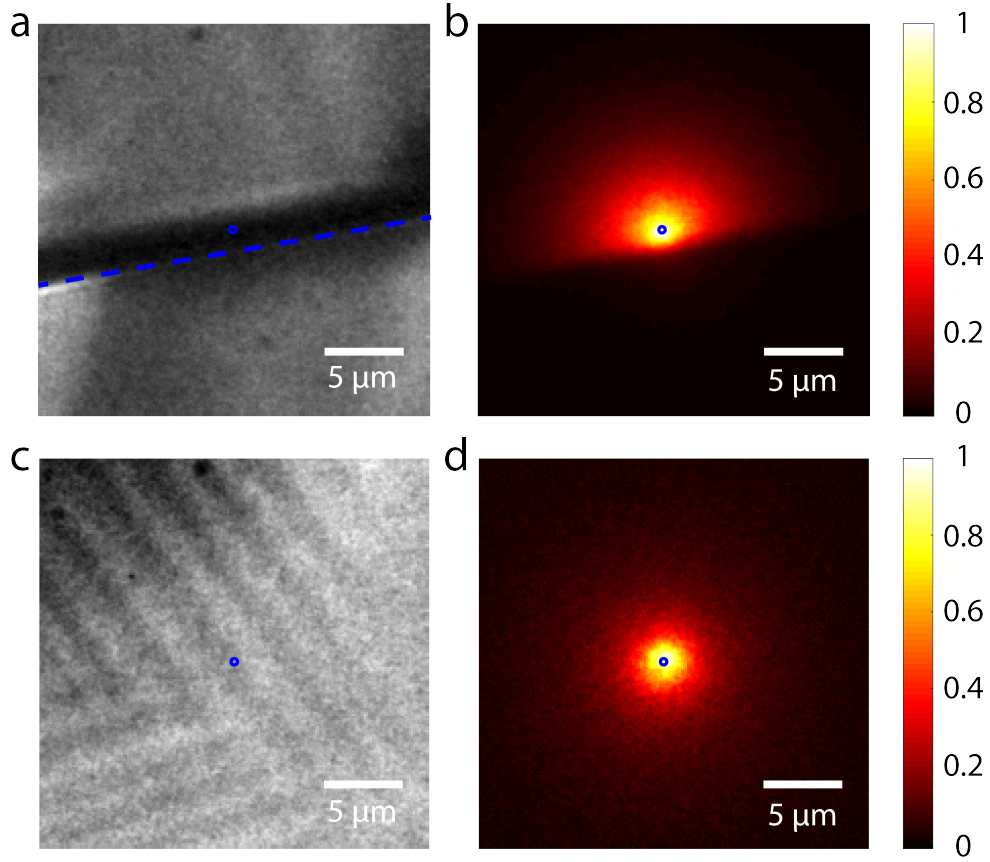


Figure 5.5: **Comparison of carrier transport across FTBs and grain boundaries via photoluminescence (PL) imaging.** (a) Optical microscopy image and (b) the corresponding PL intensity image of a MAPbI_3 multi-crystal sample with GBs. The PL excitation position is indicated by the blue point. (c) Polarized optical microscopy image and (d) the corresponding PL intensity image of a MAPbI_3 single crystal sample with a TB.

flat surfaces that were well adhered to the cover glass.

We first performed measurements on a multi-crystalline MAPbI_3 sample with grain boundaries to find out the effect of regular GBs on the carrier transport. Samples with a grain size significantly larger than the optical resolution are needed for this measurement. These samples were grown by spreading a 1.5 M MAPbI_3 gamma-butyrolactone (GBL) solution onto a hydrophobic-treated cover glass followed by slow solvent evaporation at 100 °C. This method produced large grains with lateral sizes from 0.1 to 1 mm, forming GBs between two adjacent

crystals. An example GB is indicated by the blue dashed line in Fig. 5.5(a). Figure 5.5(b) shows a PL intensity image acquired when the laser is focused on one side of the GB. By superimposing the PL intensity data and the surface photographic image, PL intensity was seen to drop abruptly across GBs, indicating that GBs can block at least one type of charge carrier. The blocking of carriers can be explained by the presence of band bending at the grain boundaries, as illustrated in Fig. 5.6, which blocks one type of carrier while extracting the other type at the grain boundaries. Such band bending at grain boundary areas has been frequently observed in Kelvin probe microscopy. [66] The band bending at GBs can be induced by self-doping of perovskites due to composition non-uniformity.

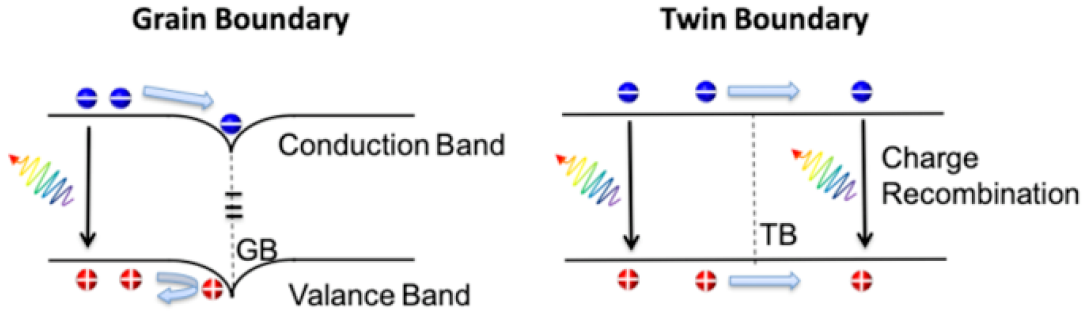


Figure 5.6: The proposed energetic diagram of MAPbI₃ with GBs (left panel) or FTBs (right panel) exhibiting the origin of their different impacts on charge carrier transport and recombination.

We then conducted PL mapping measurements on a MAPbI₃ single crystal sample with FTBs as identified in the polarized optical microscope image (Fig. 5.5(c)). The corresponding PL imaging shown in Fig. 5.5(d) presents a symmetrical intensity distribution with the diameter considerably larger than the focused excitation laser spot. The continuous PL intensity distribution across the FTBs indicates that neither electrons nor holes are blocked by the FTBs during their transportation.

5.2.3 Confocal Photoluminescence Spectroscopy for Studying Carrier Recombination

To study the impact of FTBs on carrier recombination kinetics, scanning confocal microscopy was performed to record time-resolved PL emission across the sample. PL intensity and PL recombination lifetime were mapped on the single crystals with FTBs. As shown in Fig. 5.7(a), the PL intensity shows a distribution with the stripe patterns corresponding to the ferroelastic domains, with the variation of PL intensity being less than 5%. We speculate this PL intensity variation might come from minor spatial differences in the absorption of the pump laser.

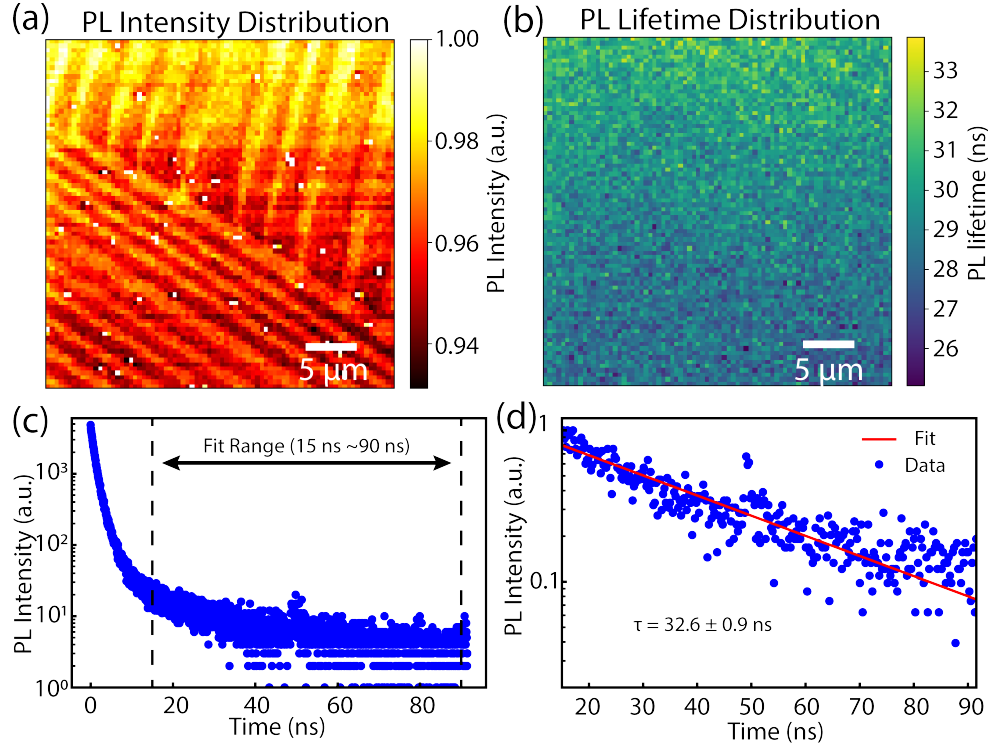


Figure 5.7: **Impact of FTBs on charge carrier recombination probed scanning confocal microscopy.** Confocal PL intensity mapping (a) and lifetime mapping (b) of FTBs. (c) Time-resolved PL intensity data and (d) single exponential fitting overlaid on the 15 ns to 90 ns time range.

An example of the time-resolved PL intensity data is shown in Fig. 5.7(c), where both a fast decay (0 to 20 ns) and a slow decay (after 20 ns) can be observed. As was discussed in Chapter

3, the initial fast drop of PL intensity might come from fast carrier decay channels (bi-molecular and Auger recombination) or carriers diffusing out of the collection area. In order to estimate the trap-assisted recombination (mono-molecular recombination), the 20 ns to 90 ns time range was fitted with a single exponential decay model. In this time range, carrier concentration is relatively low and its distribution is more homogeneous, so that the PL intensity decay mainly reflects the trap assistant recombination.

As is shown in Fig. 5.7(a,b), no significant drop of PL intensity or PL lifetime was observed at the FTBs, which suggests that FTBs do not provide additional non-radiative recombination centers.

5.3 Conclusion

The different carrier transport and recombination behaviors of GBs and FTBs might be related to their difference in defect densities. GBs in perovskite materials are often high-angle boundaries and are associated with many defects that could serve as non-radiative recombination sites. The defects accumulation near the GBs can also cause band bending which results in impeding carrier transport. On the other hand, twin boundaries are not necessarily associated with defects and thus have little effect on carrier transport and recombination.

Chapter 6

Conclusion

In this thesis, we studied the structural and optoelectronic properties of perovskite materials using photoluminescence spectroscopy methods. We observed an optical annealing effect in a mixed halide $\text{MAPbI}_x\text{Br}_{3-x}$ that improves optical quality and photostability. Given that the photo segregation mechanism of this type of perovskites is still unclear, this optical annealing effect provides a new observation for evaluating the currently available photo segregation theories. However, we could not reproduce this effect reliably on all the samples, and the mechanism for the optical annealing effect is not yet fully understood.

We established a time-resolved photoluminescence imaging method for studying carrier diffusion in FAPbI_3 perovskite thin films. This method can capture the PL evolution with a diffraction limited spatial resolution and a sub-nanosecond (500 ps) temporal resolution. Carrier diffusivity was estimated with this method and was found to increase with added background carrier densities, which is discussed in the context of trap-carrier interactions. Our result shows that the carrier transport in FAPbI_3 under one sun illumination is in a trap-limited regime, which suggests that this material still has potential for further improvement in power conversion efficiency.

Given that PL intensity is related to the local carrier concentration, this PL imaging method is proved useful for identifying carrier transport barriers in perovskite materials. We revealed

sub-grain special boundaries in FAPbI_3 perovskite thin films which restrict carrier diffusion and serve as non-radiative recombination sites. Furthermore, these sub-grain boundaries cannot be observed by conventional surface morphology characterization methods such as AFM or SEM. The existence of such boundaries may help explain why the performance of perovskite solar cells has not scaled with apparent grain size. This PL imaging method was also used to study carrier transport across ferroelastic twin boundaries in MAPbI_3 . Different from the grain boundaries and the sub-grain boundaries in FAPbI_3 , the ferroelastic twin boundaries do not impede carrier transport nor introduce non-radiative recombination channels.

In this thesis we discussed carrier transport in two kinds of boundaries that have the characteristics of twin boundaries. However, carrier transport across them was found to be very different. Further investigation is required to study the differences in carrier transport in these two types of boundaries. We also discussed methods to measure diffusivity within grains, but carrier transport across grain boundaries was only described qualitatively. An interesting extension of the methods presented here would be one that allows quantifying the resistance to carrier transport across grain boundaries.

Bibliography

- [1] Mark T. Weller, Oliver J. Weber, Jarvist M. Frost, and ron Walsh. Cubic perovskite structure of black formamidinium lead iodide, α -[hc(nh₂)₂]pb₂i₃, at 298 k. *The Journal of Physical Chemistry Letters*, 6(16):3209–3212, 2015. doi: 10.1021/acs.jpcllett.5b01432. URL <https://doi.org/10.1021/acs.jpcllett.5b01432>.
- [2] Martin A. Green, Anita Ho-Baillie, and Henry J. Snaith. The emergence of perovskite solar cells. *Nature Photonics*, 8:506, 2014. doi: 10.1038/nphoton.2014.134. URL <https://doi.org/10.1038/nphoton.2014.134>.
- [3] Eric T. Hoke, Daniel J. Slotcavage, Emma R. Dohner, Andrea R. Bowring, Hemamala I. Karunadasa, and Michael D. McGehee. Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. *Chem. Sci.*, 6:613–617, 2015. doi: 10.1039/C4SC03141E. URL <http://dx.doi.org/10.1039/C4SC03141E>.
- [4] Federico Brivio, Clovis Caetano, and Aron Walsh. Thermodynamic origin of photoinstability in the ch₃nh₃pb(i_{1-x}br_x)₃ hybrid halide perovskite alloy. *The Journal of Physical Chemistry Letters*, 7(6):1083–1087, 2016. doi: 10.1021/acs.jpcllett.6b00226. URL <https://doi.org/10.1021/acs.jpcllett.6b00226>. PMID: 26952337.
- [5] Princeton Instruments. PI-MAX4 Camera System. <ftp://ftp.piaccton.com/Public/Manuals/Princeton%20Im> 2019. [Online; accessed 04-Aug-2019].

- [6] Na Liu and ChiYung Yam. First-principles study of intrinsic defects in formamidinium lead triiodide perovskite solar cell absorbers. *Phys. Chem. Chem. Phys.*, 20:6800–6804, 2018. doi: 10.1039/C8CP00280K. URL <https://pubs.rsc.org/en/content/articlehtml/2018/cp/c8cp00280k>.
- [7] K. Lu. Stabilizing nanostructures in metals using grain and twin boundary architectures. *Nature Reviews Materials*, 1:16019, 2016. doi: 10.1038/natrevmats.2016.19. URL <https://doi.org/10.1038/natrevmats.2016.19>.
- [8] Mathias Uller Rothmann, Wei Li, Ye Zhu, Udo Bach, Leone Spiccia, Joanne Etheridge, and Yi-Bing Cheng. Direct observation of intrinsic twin domains in tetragonal $\text{ch}_3\text{nh}_3\text{pb}_3$. *Nat. Commun.*, 8:14547, 2017. doi: 10.1038/ncomms14547. URL <http://dx.doi.org/10.1038/ncomms14547>.
- [9] Evgheni Strelcov, Qingfeng Dong, Tao Li, Jungseok Chae, Yuchuan Shao, Yehao Deng, Alexei Gruverman, Jinsong Huang, and Andrea Centrone. $\text{Ch}_3\text{nh}_3\text{pb}_3$ perovskites: Ferroelasticity revealed. *Science Advances*, 3(4), 2017. doi: 10.1126/sciadv.1602165.
- [10] NREL. National renewable energy laboratory (nrel), best research-cells efficiencies chart, 2019. URL <https://www.nrel.gov/pv/assets/pdfs/best-reserch-cell-efficiencies.20190411.pdf>. [Online; accessed April-2019].
- [11] Michael Saliba, Taisuke Matsui, Ji-Youn Seo, Konrad Domanski, Juan-Pablo Correa-Baena, Mohammad Khaja Nazeeruddin, Shaik M. Zakeeruddin, Wolfgang Tress, Antonio Abate, Anders Hagfeldt, and Michael Grätzel. Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy Environ. Sci.*, 9:1989–1997, 2016. doi: 10.1039/C5EE03874J. URL <http://dx.doi.org/10.1039/C5EE03874J>.

- [12] Sabine KÄrbel, Miguel A. L. Marques, and Silvana Botti. Stability and electronic properties of new inorganic perovskites from high-throughput ab initio calculations. *J. Mater. Chem. C*, 4:3157–3167, 2016. doi: 10.1039/C5TC04172D. URL <http://dx.doi.org/10.1039/C5TC04172D>.
- [13] Ziran Zhao, Feidan Gu, Yunlong Li, Weihai Sun, Senyun Ye, Haixia Rao, Zhiwei Liu, Zuqiang Bian, and Chunhui Huang. Mixed-organic-cation tin iodide for lead-free perovskite solar cells with an efficiency of 8.12%. *Advanced Science*, 4(11):1700204, 2017. doi: 10.1002/advs.201700204. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/advs.201700204>.
- [14] Pengyang Wang, Xingwang Zhang, Yuqin Zhou, Qi Jiang, Qiufeng Ye, Zema Chu, Xingxing Li, Xiaolei Yin Yang, Zhigang, and Jingbi You. Solvent-controlled growth of inorganic perovskite films in dry environment for efficient and stable solar cells. *Nature Communications*, 9(1):2225, Jun. 2018. doi: 10.1038/s41467-018-04636-4.
- [15] Neha Arora, M. Ibrahim Dar, Alexander Hinderhofer, Norman Pellet, Frank Schreiber, Shaik Mohammed Zakeeruddin, and Michael Grätzel. Perovskite solar cells with cuscN hole extraction layers yield stabilized efficiencies greater than 20%. *Science*, 358(6364):768–771, 2017. ISSN 0036-8075. doi: 10.1126/science.aam5655. URL <https://science.sciencemag.org/content/358/6364/768>.
- [16] Lei Meng, Jingbi You, and Yang Yang. Addressing the stability issue of perovskite solar cells for commercial applications. *Nature Communications*, 9(1):5265, 12 2018. doi: 10.1038/s41467-018-07255-1.
- [17] Zhengguo Xiao, Qingfeng Dong, Cheng Bi, Yuchuan Shao, Yongbo

- Yuan, and Jinsong Huang. Solvent annealing of perovskite-induced crystal growth for photovoltaic-device efficiency enhancement. *Advanced Materials*, 26(37):6503–6509, 2014. doi: 10.1002/adma.201401685. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201401685>.
- [18] Yuanyuan Zhou, Onkar S. Game, Shuping Pang, and Nitin P. Padture. Microstructures of organometal trihalide perovskites for solar cells: Their evolution from solutions and characterization. *The Journal of Physical Chemistry Letters*, 6(23):4827–4839, 2015. doi: 10.1021/acs.jpcllett.5b01843. URL <https://doi.org/10.1021/acs.jpcllett.5b01843>. PMID: 26560696.
- [19] M.S. Jamal, M.S. Bashar, A.K. Mahmud Hasan, Zeyad A. Almutairi, Hamad F. Alharbi, Nabeel H. Alharthi, Mohammad R. Karim, H. Misran, Nowshad Amin, Kamaruzzaman Bin Sopian, and Md. Akhtaruzzaman. Fabrication techniques and morphological analysis of perovskite absorber layer for high-efficiency perovskite solar cell: A review. *Renewable and Sustainable Energy Reviews*, 98:469 – 488, 2018. ISSN 1364-0321. doi: <https://doi.org/10.1016/j.rser.2018.09.016>. URL <http://www.sciencedirect.com/science/article/pii/S1364032118306646>.
- [20] Jun Hong Noh, Sang Hyuk Im, Jin Hyuck Heo, Tarak N. Mandal, and Sang Il Seok. Chemical management for colorful, efficient, and stable inorganic–organic hybrid nanostructured solar cells. *Nano Letters*, 13(4):1764–1769, 2013. doi: 10.1021/nl400349b. URL <https://doi.org/10.1021/nl400349b>. PMID: 23517331.
- [21] Seog Joon Yoon, Sergiu Draguta, Joseph S. Manser, Onise Sharia, William F. Schneider, Masaru Kuno, and Prashant V. Kamat. Tracking iodide and bromide ion segregation in mixed halide lead perovskites during photoirradiation. *ACS Energy Letters*, 1(1):290–296, 2016. doi: 10.1021/acsenerylett.6b00158. URL <https://doi.org/10.1021/acsenerylett.6b00158>.

- [22] Connor G. Bischak, Craig L. Hetherington, Hao Wu, Shaul Aloni, D. Frank Ogle-tree, David T. Limmer, and Naomi S. Ginsberg. Origin of reversible photoinduced phase separation in hybrid perovskites. *Nano Letters*, 17(2):1028–1033, 2017. doi: 10.1021/acs.nanolett.6b04453. URL <https://doi.org/10.1021/acs.nanolett.6b04453>. PMID: 28134530.
- [23] Alex J. Barker, Aditya Sadhanala, Felix Deschler, Marina Gandini, Satyaprasad P. Senanayak, Phoebe M. Pearce, Edoardo Mosconi, Andrew J. Pearson, Yue Wu, Ajay Ram Srimath Kandada, Tomas Leijtens, Filippo De Angelis, Si  n E. Dutton, Annamaria Petrozza, and Richard H. Friend. Defect-assisted photoinduced halide segregation in mixed-halide perovskite thin films. *ACS Energy Letters*, 2(6):1416–1424, 2017. doi: 10.1021/ac-senergylett.7b00282. URL <https://doi.org/10.1021/ac-senergylett.7b00282>.
- [24] Zhibin Yang, Adharsh Rajagopal, Sae Byeok Jo, Chu-Chen Chueh, Spencer Williams, Chun-Chih Huang, John K. Katahara, Hugh W. Hillhouse, and Alex K.-Y. Jen. Stabilized wide bandgap perovskite solar cells by tin substitution. *Nano Letters*, 16(12):7739–7747, 2016. doi: 10.1021/acs.nanolett.6b03857. URL <https://doi.org/10.1021/acs.nanolett.6b03857>. PMID: 27960463.
- [25] Nam Joong Jeon, Jun Hong Noh, Young Chan Kim, Woon Seok Yang, Seungchan Ryu, and Sang Il Seok. Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells. *Nature Materials*, 13:897 EP –, Jul 2014. URL <https://doi.org/10.1038/nmat4014>. Article.
- [26] Sneha A. Kulkarni, Tom Baikie, Pablo P. Boix, Natalia Yantara, Nripan Mathews, and Subodh Mhaisalkar. Band-gap tuning of lead halide perovskites using a sequential deposition process. *J. Mater. Chem. A*, 2:9221–9225, 2014. doi: 10.1039/C4TA00435C. URL <http://dx.doi.org/10.1039/C4TA00435C>.

- [27] Laura M. Herz. Charge-carrier mobilities in metal halide perovskites: Fundamental mechanisms and limits. *ACS Energy Letters*, 2(7):1539–1548, Jul 2017. doi: 10.1021/acsenenergylett.7b00276. URL <https://doi.org/10.1021/acsenenergylett.7b00276>.
- [28] Dong Shi, Valerio Adinolfi, Riccardo Comin, Mingjian Yuan, Erkki Alarousu, Andrei Buin, Yin Chen, Sjoerd Hoogland, Alexander Rothenberger, Khabiboulakh Katsiev, Yaroslav Losovyj, Xin Zhang, Peter A. Dowben, Omar F. Mohammed, Edward H. Sargent, and Osman M. Bakr. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science*, 347(6221):519–522, 2015. ISSN 0036-8075. doi: 10.1126/science.aaa2725. URL <http://science.sciencemag.org/content/347/6221/519>.
- [29] Qingfeng Dong, Yanjun Fang, Yuchuan Shao, Padhraic Mulligan, Jie Qiu, Lei Cao, and Jinsong Huang. Electron-hole diffusion lengths $> 175 \mu\text{m}$ in solution-grown $\text{ch}_3\text{nh}_3\text{pb}\text{i}_3$ single crystals. *Science*, 347(6225):967–970, 2015. ISSN 0036-8075. doi: 10.1126/science.aaa5760. URL <http://science.sciencemag.org/content/347/6225/967>.
- [30] Makhsud I. Saidaminov, Ahmed L. Abdelhady, Banavoth Murali, Erkki Alarousu, Victor M. Burlakov, Wei Peng, Ibrahim Dursun, Lingfei Wang, Yao He, Giacomo Maculan, Alain Goriely, Tom Wu, Omar F. Mohammed, and Osman M. Bakr. High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization. *Nature Communications*, 6:7586, Jul 2015. URL <https://doi.org/10.1038/ncomms8586>. Article.
- [31] Ayan A. Zhumekenov, Makhsud I. Saidaminov, Md Azimul Haque, Erkki Alarousu, Smritakshi Phukan Sarmah, Banavoth Murali, Ibrahim Dursun, Xiao-He Miao, Ahmed L. Abdelhady, Tom Wu, Omar F. Mohammed, and Osman M. Bakr. Formamidinium lead halide perovskite crystals with unprecedented long carrier dynamics and diffusion length. *ACS Energy Letters*, 1(1):32–37, 2016. doi: 10.1021/acsenenergylett.6b00002. URL <https://doi.org/10.1021/acsenenergylett.6b00002>.

- [32] Giacomo Maculan, Arif D. Sheikh, Ahmed L. Abdelhady, Makhsud I. Saidaminov, Md Azimul Haque, Banavoth Murali, Erkki Alarousu, Omar F. Mohammed, Tom Wu, and Osman M. Bakr. $ch_3nh_3pbcl_3$ single crystals: Inverse temperature crystallization and visible-blind uv-photodetector. *The Journal of Physical Chemistry Letters*, 6(19):3781–3786, Oct 2015. ISSN 1948-7185. doi: 10.1021/acs.jpcllett.5b01666. URL <https://doi.org/10.1021/acs.jpcllett.5b01666>.
- [33] Christian Wehrenfennig, Giles E. Eperon, Michael B. Johnston, Henry J. Snaith, and Laura M. Herz. High charge carrier mobilities and lifetimes in organolead trihalide perovskites. *Advanced Materials*, 26(10):1584–1589, 2014. doi: 10.1002/adma.201305172. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201305172>.
- [34] Giles E. Eperon, Tomas Leijtens, Kevin A. Bush, Rohit Prasanna, Thomas Green, Jacob Tse-Wei Wang, David P. McMeekin, George Volonakis, Rebecca L. Milot, Richard May, Axel Palmstrom, Daniel J. Slotcavage, Rebecca A. Belisle, Jay B. Patel, Elizabeth S. Parrott, Rebecca J. Sutton, Wen Ma, Farhad Moghadam, Bert Conings, Aslihan Babayigit, Hans-Gerd Boyen, Stacey Bent, Feliciano Giustino, Laura M. Herz, Michael B. Johnston, Michael D. McGehee, and Henry J. Snaith. Perovskite-perovskite tandem photovoltaics with optimized band gaps. *Science*, 354(6314):861–865, 2016. ISSN 0036-8075. doi: 10.1126/science.aaf9717. URL <http://science.sciencemag.org/content/354/6314/861>.
- [35] Rebecca L. Milot, Giles E. Eperon, Henry J. Snaith, Michael B. Johnston, and Laura M. Herz. Temperature-dependent charge-carrier dynamics in $ch_3nh_3pbi_3$ perovskite thin films. *Advanced Functional Materials*, 25(39):6218–6227, 2015. doi: 10.1002/adfm.201502340. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adfm.201502340>.
- [36] Carlito S. Ponseca, Tom J. Savenije, Mohamed Abdellah, Kaibo Zheng, Arkady Yartsev, Tobjörn Pascher, Tobias Harlang, Pavel Chabera, Tonu Pullerits, Andrey Stepanov, Jean-Pierre Wolf, and Villy Sundström. Organometal halide perovskite solar cell

- materials rationalized: Ultrafast charge generation, high and microsecond-long balanced mobilities, and slow recombination. *Journal of the American Chemical Society*, 136(14):5189–5192, Apr 2014. ISSN 0002-7863. doi: 10.1021/ja412583t. URL <https://doi.org/10.1021/ja412583t>.
- [37] Waqaas Rehman, Rebecca L. Milot, Giles E. Eperon, Christian Wehrenfennig, Jessica L. Boland, Henry J. Snaith, Michael B. Johnston, and Laura M. Herz. Charge-carrier dynamics and mobilities in formamidinium lead mixed-halide perovskites. *Advanced Materials*, 27(48):7938–7944, 2015. doi: 10.1002/adma.201502969. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201502969>.
- [38] Z. Guo, J. S. Manser, Y. Wan, P. V. Kamat, and L. Huang. Spatial and temporal imaging of long-range charge transport in perovskite thin films by ultrafast microscopy. *Nature Communications*, 6:7471, 2015. doi: 10.1038/ncomms8471. URL <https://www.nature.com/articles/ncomms8471>.
- [39] Andrew H. Hill, Kori E. Smyser, Casey L. Kennedy, Eric S. Massaro, and Erik M. Grumstrup. Screened charge carrier transport in methylammonium lead iodide perovskite thin films. *J. Phys. Chem. Lett.*, 8(5):948–953, 2017. doi: 10.1021/acs.jpclett.7b00046. URL <https://doi.org/10.1021/acs.jpclett.7b00046>.
- [40] Patrik Årshøj, Ramuļšas Aleksiejūšas, Saulius Miasojedovas, Saulius Nargelas, Munetomo Inoue, Chuanjiang Qin, Toshinori Matsushima, Chihaya Adachi, and Saulius Juršėnas. Two regimes of carrier diffusion in vapor-deposited lead-halide perovskites. *J. Phys. Chem. C*, 121(39):21600–21609, 2017. doi: 10.1021/acs.jpcc.7b04179. URL <https://doi.org/10.1021/acs.jpcc.7b04179>.
- [41] Patrik Årshøj, Chuanjiang Qin, Ramuļšas Aleksiejūšas, Paulius Baronas, Saulius

- Miasojedovas, Takashi Fujihara, Toshinori Matsushima, Chihaya Adachi, and Saulius Jurkašius. Diffusion enhancement in highly excited *mapbi*₃ perovskite layers with additives. *J. Phys. Chem. Lett.*, 9(12):3167–3172, 2018. doi: 10.1021/acs.jpclett.8b01155. URL <https://doi.org/10.1021/acs.jpclett.8b01155>.
- [42] Dylan H. Arias, David T. Moore, Jao van de Lagemaat, and Justin C. Johnson. Direct measurements of carrier transport in polycrystalline methylammonium lead iodide perovskite films with transient grating spectroscopy. *J. Phys. Chem. Lett.*, 9(19):5710–5717, 2018. doi: 10.1021/acs.jpclett.8b02245. URL <https://doi.org/10.1021/acs.jpclett.8b02245>.
- [43] Zhenkun Guo, Ninghao Zhou, Olivia F. Williams, Jun Hu, Wei You, and Andrew M. Moran. Imaging carrier diffusion in perovskites with a diffractive optic-based transient absorption microscope. *J. Phys. Chem. C*, 122(19):10650–10656, 2018. ISSN 0036-8075. doi: 10.1021/acs.jpcc.8b03643. URL <https://doi.org/10.1021/acs.jpcc.8b03643>.
- [44] Wenming Tian, Chunyi Zhao, Jing Leng, Rongrong Cui, and Shengye Jin. Visualizing carrier diffusion in individual single-crystal organolead halide perovskite nanowires and nanoplates. *J. Am. Chem. Soc.*, 137(39):12458–12461, 2015. doi: 10.1021/jacs.5b08045. URL <https://doi.org/10.1021/jacs.5b08045>.
- [45] Wenming Tian, Jing Leng, Chunyi Zhao, and Shengye Jin. Long-distance charge carrier funneling in perovskite nanowires enabled by built-in halide gradient. *J. Am. Chem. Soc.*, 139(2):579–582, 2015. doi: 10.1021/jacs.6b10512. URL <https://doi.org/10.1021/jacs.6b10512>.
- [46] Richard Ciesielski, Frank Schädler, Nicolai F. Hartmann, Naja Giesbrecht, Thomas Bein, Pablo Docampo, and Achim Hartschuh. Grain boundaries act as solid walls for charge carrier diffusion in large crystal mapi thin films. *ACS Appl. Mater. Interfaces*, 10(9):7974–7981, 2018. doi: 10.1021/acsami.7b17938. URL <https://doi.org/10.1021/acsami.7b17938>.

- [47] Izuru Karimata, Kaoru Ohta, Yasuhiro Kobori, and Takashi Tachikawa. Several orders of magnitude difference in charge-transfer kinetics induced by localized trapped charges on mixed-halide perovskites. *ACS Appl. Mater. Interfaces*, 10(43):37057–37066, 2018. doi: 10.1021/acsami.8b13346. URL <https://doi.org/10.1021/acsami.8b13346>.
- [48] Woon Seok Yang, Jun Hong Noh, Nam Joong Jeon, Young Chan Kim, Seungchan Ryu, Jangwon Seo, and Sang Il Seok. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*, 348(6240):1234–1237, 2015. ISSN 0036-8075. doi: 10.1126/science.aaa9272. URL <http://science.sciencemag.org/content/348/6240/1234>.
- [49] Srinivas K. Yadavalli, Yuanyuan Zhou, and Nitin P. Padture. Exceptional grain growth in formamidinium lead iodide perovskite thin films induced by the δ -to- α phase transformation. *ACS Energy Lett.*, 3(1):63–64, 2018. doi: 10.1021/acsenerylett.7b01150. URL <https://doi.org/10.1021/acsenerylett.7b01150>.
- [50] Krzysztof Galkowski, Anatolie Mitiglu, Atsuhiko Miyata, Paulina Plochocka, Oliver Portugall, Giles E. Eperon, Jacob Tse-Wei Wang, Thomas Stergiopoulos, Samuel D. Stranks, Henry J. Snaith, and Robin J. Nicholas. Determination of the exciton binding energy and effective masses for methylammonium and formamidinium lead tri-halide perovskite semiconductors. *Energy Environ. Sci.*, 9:962–970, 2016. doi: 10.1039/C5EE03435C. URL <http://dx.doi.org/10.1039/C5EE03435C>.
- [51] Jun-Fei Wang, Xiao-Nan Fu, and Jun-Tao Wang. First-principles analysis of the structural, electronic, and elastic properties of cubic organic–inorganic perovskite $\text{hc}(\text{nh}_2)_2\text{pb}i_3$. *Chinese Physics B*, 26(10):106301, sep 2017. doi: 10.1088/1674-1056/26/10/106301.
- [52] Giacomo Giorgi, Jun-Ichi Fujisawa, Hiroshi Segawa, and Koichi Yamashita. Small photocarrier effective masses featuring ambipolar transport in methylammonium lead iodide

- perovskite: A density functional analysis. *The Journal of Physical Chemistry Letters*, 4(24): 4213–4216, 2013. doi: 10.1021/jz4023865. URL <https://doi.org/10.1021/jz4023865>.
- [53] W. Shockley and W. T. Read. Statistics of the recombinations of holes and electrons. *Phys. Rev.*, 87:835–842, Sep 1952. doi: 10.1103/PhysRev.87.835. URL <https://link.aps.org/doi/10.1103/PhysRev.87.835>.
- [54] J.G. Simmons and G.W Taylor. Nonequilibrium steady-state statistics and associated effects for insulators and semiconductom containing an arbitrary distribution of traps. *Physical Review B*, 4:502–511, July 1971.
- [55] G. Xing, N. Mathews, S. S. Lim, N. Yantara, D. Liu, X. Sabba, M. GrÃd’tzel, S Mhaisalkar, and T. C Sum. Low-temperature solution-processed wavelength-tunable perovskites for lasing. *Nature Materials*, 13:476–480, March 2014.
- [56] Yuanyuan Zhou, Onkar S. Game, Shuping Pang, and Nitin P. Padture. Microstructures of organometal trihalide perovskites for solar cells: Their evolution from solutions and characterization. *J. Phys. Chem. Lett.*, 6(23):4827–4839, 2015. doi: 10.1021/acs.jpcllett.5b01843. URL <https://pubs.acs.org/doi/abs/10.1021/acs.jpcllett.5b01843>. PMID: 26560696.
- [57] C. V. Thompson. Structure evolution during processing of polycrystalline films. *Annu. Rev. Mater. Sci.*, 30(1):159–190, 2000. doi: 10.1146/annurev.matsci.30.1.159. URL <https://doi.org/10.1146/annurev.matsci.30.1.159>.
- [58] Willam E. Lee and W. Mark Rainforth. *Ceramic Microstructures*. CHAPMAN & HALL, 1994.
- [59] Dane W. deQuilettes, Sarthak Jariwala, Sven Burke, Mark E. Ziffer, Jacob T.-W. Wang, Henry J. Snaith, and David S. Ginger. Tracking photoexcited carriers

- in hybrid perovskite semiconductors: Trap-dominated spatial heterogeneity and diffusion. *ACS Nano*, 11(11):11488–11496, 2017. doi: 10.1021/acsnano.7b06242. URL <https://doi.org/10.1021/acsnano.7b06242>. PMID: 29088539.
- [60] M. Jordan Snaider, Zhi Guo, Ti Wang, Mengjin Yang, Long Yuan, Kai Zhu, and Libai Huang. Ultrafast imaging of carrier transport across grain boundaries in hybrid perovskite thin films. *ACS Energy Lett.*, 3(6):1402–1408, 2018. doi: 10.1021/acsenenergylett.8b00560. URL <https://doi.org/10.1021/acsenenergylett.8b00560>.
- [61] Michael Saliba, JuanâÃPablo CorreaâÃBaena, Michael Grätzel, Anders Hagfeldt, and Antonio Abate. Perovskite solar cells: From the atomic level to film quality and device performance. *Angew. Chem., Int. Ed. Engl.*, 57(10):2554–2569, 2018. doi: 10.1002/anie.201703226. URL <https://doi.org/10.1002/anie.201703226>.
- [62] Jinsong Huang, Yuchuan Shao, and Qingfeng Dong. Organometal trihalide perovskite single crystals: A next wave of materials for 25% efficiency photovoltaics and applications beyond? *J. Phys. Chem. Lett.*, 6(16):3218–3227, 2015. doi: 10.1021/acs.jpcllett.5b01419. URL <https://doi.org/10.1021/acs.jpcllett.5b01419>.
- [63] Zhaolai Chen, Qingfeng Dong, Ye Liu, Chunxiong Bao, Yanjun Fang, Yun Lin, Shi Tang, Qi Wang, Xun Xiao, Yang Bai, Yehao Deng, and Jinsong Huang. Thin single crystal perovskite solar cells to harvest below-bandgap light absorption. *Nature Communications*, 8:1890, 2018. doi: 10.1038/s41467-017-02039-5. URL <https://doi.org/10.1038/s41467-017-02039-5>.
- [64] Chunxiong Bao, Zhaolai Chen, Yanjun Fang, Haotong Wei, Yehao Deng, Xun Xiao, Lingliang Li, and Jinsong Huang. Low-noise and large-linear-dynamic-range photodetectors based on hybrid-perovskite thin-single-crystals. *Advanced Materials*, 29(39):1703209, 2017. doi: 10.1002/adma.201703209. URL

<https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201703209>.

- [65] Qingfeng Dong, Yongbo Yuan, Yuchuan Shao, Yanjun Fang, Qi Wang, and Jinsong Huang. Abnormal crystal growth in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ using a multi-cycle solution coating process. *Energy Environ. Sci.*, 8:2464–2470, 2015. doi: 10.1039/C5EE01179E. URL <http://dx.doi.org/10.1039/C5EE01179E>.
- [66] Jae S. Yun, Anita Ho-Baillie, Shujuan Huang, Sang H. Woo, Yooun Heo, Jan Seidel, Fuzhi Huang, Yi-Bing Cheng, and Martin A. Green. Benefit of grain boundaries in organic–inorganic halide planar perovskite solar cells. *The Journal of Physical Chemistry Letters*, 6(5):875–880, 2015. doi: 10.1021/acs.jpclett.5b00182. URL <https://doi.org/10.1021/acs.jpclett.5b00182>.