

Contents

Preface xv

1	Introduction to Perovskite	1
	<i>Tianwei Duan, Iván Mora-Seró, and Yuanyuan Zhou</i>	
1.1	Evolution of Perovskite	1
1.2	Structure of Perovskite	2
1.3	Property and Application of Perovskite	4
1.4	Summary and Outlook	7
	References	7
2	Halide Perovskite Single Crystals	9
	<i>Clara Aranda-Alonso and Michael Saliba</i>	
2.1	Introduction	9
2.2	Crystal Structure	9
2.2.1	Lead-Based Perovskite Single Crystals	10
2.2.2	Lead-Free Perovskite Single Crystals	12
2.2.3	All-Inorganic Perovskite Single Crystals	13
2.3	Synthesis Methods	14
2.3.1	Antisolvent Vapor-Assisted Crystallization (AVC) Method	14
2.3.2	Solution Temperature Lowering (STL) Method	15
2.3.3	Bridgman Method	16
2.3.4	Slow Evaporation Method	17
2.3.5	Inverse Temperature Crystallization (ITC) Method	19
2.3.6	Methods for 2D and 1D Perovskite Single Crystals	20
2.4	Optoelectronic Properties of Halide Perovskite Single Crystals	21
2.4.1	UV-Vis Absorption, Photoluminescence (PL), and Transient Decays: TRPL and TPV	21
2.4.2	Electronic Properties	23
2.4.2.1	Space-Charge-Limited Current (SCLC)	23
2.4.2.2	Impedance Spectroscopy (IS)	26
2.5	Applications	29
2.5.1	Photodetectors	29
2.5.2	X-Ray Detection	30

- 2.5.3 γ -Ray Detection and Scintillators 30
- 2.5.4 Solar Cells 32
- 2.5.5 Light Emitting Diodes 38
- 2.5.6 Memristors 41
- Acknowledgments 43
- References 43

3 Halide Perovskite Nanocrystals 49

Samrat Das Adhikari, Andrés F. Gualdrón-Reyes, and Iván Mora-Seró

- 3.1 Introduction 49
- 3.2 Methodology 51
 - 3.2.1 Hot-injection (HI) Method 51
 - 3.2.2 Ligand-assisted Reprecipitation (LARP) Method 54
 - 3.2.3 Microwave-assisted Synthesis 55
 - 3.2.4 Ball-milling Process 55
- 3.3 Quantum Confinement Effect 57
 - 3.3.1 Nanocubes 57
 - 3.3.2 Nanoplatelets 58
 - 3.3.3 Nanowires 59
- 3.4 Solution-processed Halide Exchange 59
- 3.5 Post-synthesis Defect Recovery 61
- 3.6 Different Shapes of the Nanocrystals 62
 - 3.6.1 Shape-controlling Reaction Parameters 63
 - 3.6.1.1 Temperature 63
 - 3.6.1.2 Annealing Time 63
 - 3.6.1.3 Role of Capping-ligand 64
- 3.7 Doping in Perovskite Nanocrystals 64
 - 3.7.1 Mn²⁺ Doping 65
 - 3.7.2 Lanthanide Doping 65
 - 3.7.3 Other B-site Dopants 67
 - 3.7.4 Postsynthesis Doping 67
- 3.8 Lead-free Perovskite Nanocrystals 69
 - 3.8.1 Classifications According to the Structure and Compositions 69
 - 3.8.2 Challenges of the Lead-free Perovskites 69
- 3.9 Summary 70
- References 71

4 Dimensionality Modulation in Halide Perovskites 79

Akriti, Jee Yung Park, Shuchen Zhang, and Letian Dou

- 4.1 Classification of Low-Dimensional Perovskites 79
 - 4.1.1 Morphological Low-Dimensional Perovskites Through Size Reduction (ABX₃ Perovskites) 79
 - 4.1.2 Molecular Low-Dimensional Perovskites Through Structure Tuning (Non-ABX₃ Perovskites) 80

4.2	Synthesis and Characterization of Morphological Low-Dimensional (ABX ₃) Halide Perovskites	80
4.2.1	0D Quantum Dots	80
4.2.2	1D Nanowires	81
4.2.3	2D Nanoplatelets	82
4.3	Synthesis and Characterization of Molecular Low-Dimensional (Non-ABX ₃) Halide Perovskites	83
4.3.1	0D	83
4.3.1.1	Synthesis and Properties of 0D Perovskites	83
4.3.1.2	0D Cesium Lead Halides	87
4.3.2	1D	88
4.3.3	2D and Quasi-2D	90
4.3.3.1	Synthesis of 2D and Quasi-2D Perovskites Single Crystal	90
4.3.3.2	Synthesis of 2D and Quasi-2D Perovskites Nanocrystal	99
4.4	Applications of Low-Dimensional Halide Perovskites	101
4.5	Current Challenges and Prospects of Low-Dimensional Halide Perovskites	104
	References	106
5	Halide Double Perovskites	115
	<i>Carina Pareja-Rivera, Dulce Zugasti-Fernández, Paul Olalde-Velasco, and Diego Solís-Ibarra</i>	
5.1	Definition and Structure	116
5.2	Properties	118
5.2.1	Chemical Doping	121
5.2.2	Random Ordering	122
5.2.3	Stability	122
5.3	Applications in Solar Cells and LEDs	123
5.3.1	Photovoltaic Solar Cells	123
5.3.2	Light-Emitting Diodes (LEDs)	125
5.3.3	White-LEDs	125
5.3.4	Phosphorus	126
5.3.5	Two or More Phosphorus	126
5.4	Other Applications	126
5.4.1	Photodetectors	127
5.4.1.1	UV Detectors	128
5.4.1.2	X-Ray Detectors	128
5.4.2	Memristors	130
5.4.3	Photocatalysis	131
5.4.4	Sensors	131
5.4.5	Future Applications	132
5.5	Related Materials: Layered Double Perovskites and Vacancy Ordered Double Perovskites	132
5.5.1	Dimensional Reduction	132
5.5.2	Vacancy Ordered Perovskites	133

- 5.5.2.1 $A_2B(IV)X_6$: B(IV) Substitution + Vacancies 134
- 5.5.2.2 $A_3B(III)X_9$: B(III) Substitution + Vacancies 135
- 5.5.2.3 $A_2B(II)B_2(III)X_{12}$: B(II), B(III) Substitution + Vacancies □ 135
- 5.6 Conclusions 135
- References 136

6 Tin Halide Perovskite Solar Cells 147

Xianyuan Jiang, Zihao Zang, and Zhijun Ning

- 6.1 Introduction 147
- 6.2 Tin Perovskite Properties 148
 - 6.2.1 Crystal Structure 148
 - 6.2.2 Band Structure and Oxidation 149
 - 6.2.3 Electrical Properties and Defects 151
- 6.3 Perovskite Composition Engineering 151
 - 6.3.1 Three-Dimensional TPSC 151
 - 6.3.2 Low-Dimensional TPSC 153
- 6.4 Additives Manipulation 155
 - 6.4.1 Crystallization Regulators 155
 - 6.4.2 Deoxidizers 156
 - 6.4.3 Interfaces Passivating Materials 156
- 6.5 Device Architecture Engineering 156
 - 6.5.1 Normal and Inverted Structures 156
 - 6.5.2 Band Alignment 157
- 6.6 Conclusion 158
- References 158

7 Fundamentals and Synthesis Methods of Metal Halide Perovskite Thin Films 165

Mingwei Hao, Tanghao Liu, Yalan Zhang, Tianwei Duan, and Yuanyuan Zhou

- 7.1 Introduction 165
- 7.2 Fundamentals of MHPs Thin Films 166
 - 7.2.1 Crystal Structures and Compositions 166
 - 7.2.1.1 3D MHPs 167
 - 7.2.1.2 Lead-free MHPs 168
 - 7.2.1.3 2D MHPs 170
 - 7.2.2 Microstructures 171
 - 7.2.2.1 Types of the GBs 171
 - 7.2.2.2 Grain Size and Distribution 172
 - 7.2.2.3 Crystallographic Orientations 173
- 7.3 Thin Film Growth Mechanism 173
 - 7.3.1 Crystal Nucleation Mechanism 173
 - 7.3.1.1 Nucleation Theory 173
 - 7.3.1.2 Influences on Nucleation 176
 - 7.3.2 Crystal Growth Mechanism 176
 - 7.3.2.1 Basic Growth Theory 176

7.3.2.2	Grain-coarsening Theory	178
7.4	One-step Growth	180
7.4.1	Growth From Solutions	180
7.4.1.1	Spin-coating	180
7.4.1.2	Drop-casting	182
7.4.2	Growth from Vapor Phase	184
7.4.2.1	Thermal Evaporation	184
7.4.2.2	Pulsed Laser Deposition	185
7.5	Two-step Growth	186
7.5.1	Growth from Solutions	187
7.5.1.1	Immersion Method	187
7.5.1.2	Spin-coating Method	189
7.5.1.3	Electro/Chemical Bath Deposition	190
7.5.2	Growth From Vapor Phase	190
7.5.2.1	Vapor-assisted Solution Processing	190
7.5.2.2	Sequential Vapor Deposition	191
7.6	Scalable Growth Methods	192
7.6.1	Blade Coating	193
7.6.2	Slot-die Coating	195
7.6.3	Spray Coating	196
7.6.4	Meniscus-assisted Solution Printing	197
7.6.5	Inkjet Printing	199
7.7	Postdeposition Treatments	200
7.7.1	Annealing	200
7.7.1.1	Solvent Annealing	200
7.7.1.2	Vacuum-assisted Annealing	201
7.7.2	Organic-gas Dosing	201
7.8	Summary	203
	Acknowledgments	204
	References	204
8	First Principles Atomistic Theory of Halide Perovskites	215
	<i>Linn Leppert</i>	
8.1	Introduction: What I Talk About When I Talk About First Principles Calculations of Halide Perovskites	215
8.2	Structural Properties	217
8.2.1	A Short Introduction to Density Functional Theory	217
8.2.2	DFT Calculations in Practice	218
8.2.2.1	Approximations	218
8.2.2.2	Calculations of Structural Properties	222
8.2.3	Zero-Temperature Calculations for Halide Perovskites	223
8.2.4	Structural Dynamics	227
8.2.4.1	Molecular Dynamics: From Classical Force Fields to DFT Accuracy	227
8.2.4.2	Perovskites and the Breakdown of the Harmonic Approximation	228
8.2.4.3	A Primer on Ion Migration	229

8.3	Optoelectronic Properties	231
8.3.1	Electronic Band Structures	232
8.3.1.1	What Can DFT Tell Us About Band Gaps of Solids?	232
8.3.1.2	A Short Introduction to the GW Approach	233
8.3.1.3	The Band Structure of Halide Perovskites: A Tight-Binding Perspective	235
8.3.1.4	Toward Predictive Band Structure Calculations for Halide Perovskites	237
8.3.2	Optical Properties	239
8.3.2.1	A Short Introduction to the Bethe–Salpeter Equation Approach	239
8.3.2.2	Neutral Excitations in Halide Perovskites	240
8.4	Concluding Remarks: First Person Singular	242
	Acknowledgments	243
	References	243
9	Comparing the Charge Dynamics in MAPbBr₃ and MAPbI₃ Using Microwave Photoconductance Measurements	251
	<i>Tom J. Savenije, Jiashang Zhao, and Valentina M. Caselli</i>	
9.1	Time-Resolved Microwave Conductivity	251
9.2	Global Modeling of TRMC Data	254
9.3	TRMC Measurements on MAPbI ₃ and MAPbBr ₃	255
9.4	TRMC Measurements on MAPbI ₃ and MAPbBr ₃ with Charge Selective Contacts	258
	Acknowledgement	261
	References	261
10	Hot Carriers in Halide Perovskites	263
	<i>Jia Wei Melvin Lim, Yue Wang, and Tze Chien Sum</i>	
10.1	Introduction	263
10.1.1	Potential of Perovskites for Next-Generation Photovoltaics	264
10.2	Hot Carrier Cooling Mechanisms	265
10.3	Slow Hot Carrier Cooling in Halide Perovskites	266
10.3.1	Hot Phonon Bottleneck	266
10.3.2	Auger Heating of Hot Carriers	268
10.3.3	Large Polaron Formation	268
10.3.4	Spectroscopic Signature of Hot Carriers	269
10.3.4.1	Transient Absorption	270
10.3.4.2	Fluorescence-Based Techniques	272
10.3.5	Hot Carrier Extraction	274
10.4	Utilizing Hot Carriers in Halide Perovskites	275
10.4.1	Hot Carrier Solar Cell	275
10.4.2	Toward the Realization of Perovskite Hot Carrier Solar Cells	277
10.4.2.1	Cooling Loss to the Lattice	277
10.4.2.2	Energy Selective Contacts	279
10.4.2.3	Loss of Cold Carriers	279

10.5	Multiple Exciton Generation	280
10.5.1	MEG Metrics	281
10.6	Multiple Exciton Generation Mechanisms	283
10.6.1	The Debate Over the MEG Threshold and MEG Mechanism	283
10.6.2	Underlying Mechanism of the Efficient MEG in Perovskite	285
10.6.3	Controversy and Pitfalls Over Photocharging and Artifactual MEG Signal	287
10.7	Efficient Multiple Exciton Generation in Halide Perovskites	289
10.7.1	Low Multiple Exciton Generation Threshold	290
10.7.2	High Multiple Exciton Generation Efficiency	291
10.7.3	Large Multiple Exciton Generation Quantum Yield	291
10.7.4	Spectroscopic Signatures of Multiple Exciton Generation	292
10.7.4.1	Transient Absorption Spectroscopy	292
10.7.4.2	Photocurrent-Based Techniques	294
10.8	Utilizing Multiple Exciton Generation in Halide Perovskites	296
10.8.1	Multiple Exciton Generation Solar Cells	296
10.8.2	Potential of Multiple Exciton Generation Solar cells	298
10.9	Conclusion and Outlook	299
	References	300
11	Ionic Transport in Perovskite Semiconductors	305
	<i>Wenke Zhou, Yicheng Zhao, and Qing Zhao</i>	
11.1	Theoretical Basis of Ionic Transport	305
11.2	Characterizations of Ionic Transport	306
11.3	Mobile Ions in Perovskite Film Under Electric Field	309
11.4	The Factors Affecting Ionic Transport in Perovskites	311
11.4.1	Moisture	311
11.4.2	Light Illumination	311
11.4.3	Perovskite Composition	313
11.4.4	Grain Boundary	315
11.4.5	Lattice Strain	317
11.5	The Impact of Ionic Transport on Perovskite Films and Devices	318
11.5.1	Phase Segregation	318
11.5.2	Doping Effects	320
11.5.3	SCLC and TFT Devices	321
11.5.4	Degradation in Functional Devices	322
11.6	Summary and Outlook	322
	References	324
12	Light Emission of Halide Perovskites	329
	<i>David O. Tiede, Juan F. Galisteo-López, and Hernán Míguez</i>	
12.1	Introduction	329
12.2	Charge-Carrier Recombination in Lead-Halide Perovskites	330
12.2.1	Monomolecular Recombination	331
12.2.2	Bimolecular Recombination	334

12.2.3	Trimolecular Recombination	335
12.2.4	Recombination Constants in Excitonic Systems	336
12.2.5	Common Recombination Dynamics Measurement Techniques and Experimental Evidence	337
12.3	Photoinduced Effects on Charge Carrier Recombination	338
12.4	Lasing in Lead-Halide Perovskites	341
12.5	Conclusions	345
	References	345
13	Epitaxy and Strain Engineering of Halide Perovskites	351
	<i>Yang Hu, Jie Jiang, Lifu Zhang, Yunfeng Shi, and Jian Shi</i>	
13.1	Introduction	351
13.2	Epitaxy of Thin Film and Nanostructures	353
13.2.1	Epitaxial Substrates	353
13.2.2	Epitaxial Growth and Defects Formation Mechanisms	355
13.2.3	Experimental Progresses	358
13.3	Strain Engineering	360
13.3.1	Theoretical Progresses	361
13.3.2	Experimental Progresses	363
13.4	Opportunities and Challenges	365
	Acknowledgments	366
	References	367
14	Electron Microscopy of Perovskite Solar Cell Materials	377
	<i>Mathias U. Rothmann, Wei Li, and Zhiwei Tao</i>	
14.1	Introduction	377
14.2	Fundamentals of Electron Microscopy	377
14.3	Signal Generation	379
14.4	SEM	381
14.4.1	Cathodoluminescence	381
14.4.1.1	Comparison of CL and Photoluminescence (PL)	382
14.4.1.2	Working Principle	382
14.4.1.3	CL for Perovskites	383
14.4.2	Electron-Beam-Induced Current	387
14.4.2.1	Working Principle of EBIC	387
14.4.2.2	Applications	387
14.4.3	Electron Backscatter Diffraction	389
14.4.3.1	Differences Between EBSD, XRD, and TEM	390
14.4.3.2	Working Principle of EBSD	391
14.4.3.3	EBSD for Perovskites	392
14.4.4	TEM	395
14.4.4.1	Sample Preparation and Transfer	395
14.4.4.2	Imaging Conditions	398
14.4.4.3	Beam Damage	400
14.4.4.4	Examples of Applications of TEM	402

14.5	Conclusions	406
	Acknowledgments	407
	References	407
15	In Situ Characterization of Halide Perovskite Synthesis	411
	<i>Maged Abdelsamie, Tim Kodalle, Mriganka Singh, and Carolin M. Sutter-Fella</i>	
15.1	Introduction	411
15.2	Fundamentals of X-Ray Scattering and Fluorescence Techniques	412
15.2.1	Grazing Incidence Wide-Angle X-Ray Scattering (GIWAXS)	413
15.2.2	Grazing Incidence Small-Angle X-Ray Scattering (GISAXS)	414
15.2.3	X-Ray Fluorescence (XRF)	416
15.2.4	Selected Examples for In Situ X-Ray Scattering and Fluorescence	416
15.2.4.1	In Situ GIWAXS to Study Crystallization Kinetics and A-Site Doping	416
15.2.4.2	In Situ GIWAXS to Probe Film Evolution via Antisolvent and Gas Jet Treatments	418
15.2.4.3	In Situ X-Ray Diffraction (XRD), XRF, and GISAXS to Probe the PbCl ₂ -Derived Formation of MAPbI ₃	420
15.2.4.4	In Situ GIWAXS to Probe the 2D Perovskite Formation on 3D Films	420
15.3	In Situ Optical Spectroscopy	423
15.3.1	Fundamentals of Absorption and Emission of Light in Halide Perovskites	423
15.3.2	Setup Design for In Situ Optical Spectroscopy	425
15.3.3	Selected Examples for In Situ Optical Spectroscopy	426
15.3.3.1	Fast In Situ Reflectance Measurements to Characterize the Perovskite Formation	426
15.3.3.2	In Situ UV-Vis Absorbance Characterization During the Drying Stage	427
15.3.3.3	In Situ Photoluminescence Characterization to Investigate the Role of the Precursor	428
15.4	Examples of In Situ Multimodal Characterization During Solution-Based Fabrication	430
15.5	Probing Beam-Sample Interaction	435
15.6	Summary and Outlook	437
	Acknowledgments	437
	References	437
16	Multimodal Characterization of Halide Perovskites: From the Macro to the Atomic Scale	443
	<i>Tiarnan A. S. Doherty and Samuel D. Stranks</i>	
16.1	Introduction	443
16.2	Early Multimodal Characterization Work	445
16.3	Recent Multimodal Characterization	450
16.3.1	Subgrain Features	450

16.3.2	Strain and Photophysics	453
16.3.3	Atomic Scale Multimodal Studies	462
16.4	Pressing Challenges and Opportunities	464
16.4.1	Challenges: Beam Damage	464
16.4.2	Challenges: Resolution Limits	469
16.4.3	Challenges: Image Registration and Sample Fabrication	470
16.4.4	Challenges: Facility Access and Data Acquisition	471
16.5	Outlook and Opportunities	471
	References	475
	Index	483