Synthesis and optical study of lead halide perovskites for opto-electronic applications

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**SYNTHESIS AND OPTICAL STUDY OF LEAD
HALIDE PEROVSKITES FOR OPTO-ELECTRONIC
APPLICATIONS**

HA SON TUNG

**SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES**

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**SYNTHESIS AND OPTICAL STUDY OF LEAD
HALIDE PEROVSKITES FOR OPTO-ELECTRONIC
APPLICATIONS**

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Abstract

Organic-inorganic metal halide perovskite is an emerging class of semiconductors. In the past few years, we have witnessed many breakthrough applications of this material, especially in the field of thin film solar cells, light emitting diodes, and lasers. The perovskite (ABX_3 or A_2BX_4) is a rich family of material with thousands of possible compositions by changing either: organic component (A), metal (B), or halogen (X). These perovskite compounds are famous for their numbers of excellent optical and electrical properties such as: high absorption coefficient, long carrier diffusion length, low defect density, good carrier mobility, and so on. In addition, the bandgap of the material can be tuned from ultraviolet to near infrared by simply changing the chemical composition. With the ease of low-temperature solution process-ability and abundance of the sourced materials, the perovskite is rapidly becoming a strong candidate for many practical applications in optoelectronics.

In the early day of perovskite research, the most conventional method to prepare sample is via either spin-coating or thermal evaporation method. These methods usually result in polycrystalline film with many pin-holes and defects. As a physicist, my first aim is to find a way to prepare highest quality, single crystal samples for studying their intrinsic and fundamental properties. I have utilized Chemical Vapor Deposition (CVD) method to grow single crystal perovskites. This method has advantages over other single crystal growth methods such as: gas-phase reaction without solvent which can cause residuals or byproducts, inert growth environment, good reproducibility, and highly controllable growth parameters. Indeed, I have developed a facile two-step method to prepare nanoplatelets and nanowires of the perovskite which will be presented in Chapter 3. I also used solution growth method to prepare two dimensional

perovskite crystals and mechanical exfoliation to prepare the perovskite flake for optical measurements.

In Chapter 4, I will present the fundamental study on optical properties of the perovskite such as: absorption and photoluminescence properties, measurement of carrier diffusion length, phase transition, and phonon-assisted upconversion photoluminescence. Variety of optical instruments were employed to study in this thesis such as: Micro-Raman spectroscopy (Horiba T64000), micro-UV-VIS transmission spectroscopy (CRAIC20), time-resolved photoluminescence spectroscopy, femto-second laser system (Spectra-Physics), *etc.* The fundamental study of the material at the beginning has led to some important applications in optically pumped laser and laser cooling. The excellent optical properties of the perovskite crystals compared to conventional film sample also confirmed the high quality of samples grown by my method.

Chapter 5 is devoted for optically pumped lasing application in the perovskite single crystals. In this chapter, the lasing behavior of several materials will be discussed in detail such as: layered PbI_2 (*i.e.*, precursor of perovskite), 3D perovskite nanoplatelets, and 2D perovskite flake. In most cases, the lasing mechanism was attributed to whispering gallery mode (WGM) cavity which was naturally formed in the crystal. Indeed, my work on room temperature, near infrared lasing of $\text{CH}_3\text{NH}_3\text{PbX}_3$ nanoplatelets published in *Nano Letters* is the very first reports on lasing of this material. The observation of lasing in 2D perovskite flake was not achieved before.

Finally, I will present the experimental demonstration of laser cooling in perovskite. The material has been known to have strong electron/exciton-phonon interaction in the literature. In the study of the material optical properties, I have discovered that both 2D

and 3D perovskites have super strong phonon-assisted upconversion photoluminescence, a critical condition to achieve laser cooling in semiconductor. By carefully design experiment and sample fabrication, I were able to achieve net laser cooling in the material and substantially extend the toolbox for future application of the field.

In conclusion, my thesis presented a complete study on high quality single crystal lead halide perovskites. In the synthesis part, I have introduced a facile method to obtain high crystalline perovskite nanoplatelets and nanowires using a home-build CVD setup. Using these crystals and optical spectroscopy, important fundamental properties of lead halide perovskite were studied such as: carrier diffusion length, temperature-dependent band gap shift, phonon-assisted upconversion photoluminescence behavior, *etc.* These crystals were then used as WGM optical cavity to achieve lasing at room temperature. Laser cooling in perovskite was also demonstrated for the first time.

Table of contents

Acknowledgment	i
Abstract	ii
List of abbreviations	ix
Citations to published works	x
Chapter 1 : Introduction.....	1
1.1 Perovskite materials	1
1.2 Synthesis of low dimensional perovskite single crystals	4
1.2.1 Perovskite quantum dot.....	5
1.2.2 Perovskite nanowires	10
1.2.3 Perovskite nanoplatelets.....	14
1.3 Optical properties of perovskite nanocrystals	20
1.3.1 Band structure of perovskite	20
1.3.2 Bandgap tunability	22
1.3.3 Photoluminescence quantum efficiency	23
1.3.4 Quantum confinement effect.....	24
1.4 Applications of perovskite beyond solar cell	25
1.4.1 Optically pumped lasing in perovskite	25
1.4.2 Light emitting diode.....	27
1.4.3 Other applications	28
1.5 Motivation and Objectives of this thesis	29

1.6	Organization of the thesis.....	31
Chapter 2	: Instrumentation	34
2.1	Chemical vapor deposition.....	34
2.2	Transmission and reflectance micro-spectroscopy	36
2.3	Raman/photoluminescence spectroscopy.....	41
2.4	Excitation lasers	43
Chapter 3	: Synthesis and characterization of low dimensional perovskite single crystals	45
3.1	CVD synthesis of lead halide nanoplatelets	46
3.2	Controlled growth of PbBr ₂ nanowire array	53
3.3	Conversion of lead halide to perovskite.....	58
3.4	Solution synthesis and mechanical exfoliation of 2D perovskites.....	65
3.5	Summary	67
Chapter 4	: Optical properties of low dimensional perovskite crystals.....	69
4.1	Diffusion length measurement in single CH ₃ NH ₃ PbI ₃ nanoplatelet	69
4.2	Abnormal bandgap shift and phase transition in CH ₃ NH ₃ PbI ₃ nanoplatelet	72
4.3	Exciton binding energy in CH ₃ NH ₃ PbI ₃ nanoplatelet.....	80
4.4	Phonon assisted upconversion photoluminescence in perovskite.....	82
4.5	Summary	84
Chapter 5	: Lasing in perovskite nanoplatelets.....	85
5.1	Introduction	85
5.1.1	Introduction to nano/micro-laser.....	85

5.1.2	Whispering gallery mode (WGM) cavity	88
5.2	Lasing in layered material – PbI ₂ nanoplatelets	91
5.2.1	Lasing in PbI ₂ nanoplatelets.....	93
5.2.2	Lasing mechanism and intrinsic properties of PbI ₂ nanoplatelet.....	97
5.2.3	Thickness-dependent lasing in PbI ₂ nanoplatelets	100
5.3	Room temperature NIR lasing in 3D perovskite nanoplatelets.....	104
5.3.1	Lasing results of CH ₃ NH ₃ PbI _{3-a} X _a nanoplatelets.....	105
5.3.2	WGM analysis of perovskite nanoplatelets	107
5.3.3	Integration of perovskite laser onto different substrates.....	110
5.4	Lasing in layered perovskites	111
5.4.1	Lasing results in 2D perovskites	114
5.4.2	Exciton origin and trap-state in single crystal 2D perovskite.....	115
5.4.3	Lasing in 2D-3D hybrid perovskites.....	118
5.5	Summary	121
Chapter 6: Laser cooling in perovskite single crystals		123
6.1	Introduction to laser cooling	123
6.2	Experiment method	128
6.2.1	Experiment setup and temperature measurement method	128
6.2.2	Photoluminescence versus temperature calibration in perovskites.....	131
6.3	Laser cooling in CH ₃ NH ₃ PbI ₃ nanoplatelet	134
6.3.1	Laser cooling results	134

6.3.2	Laser cooling origin in perovskite	135
6.3.3	Thickness dependence cooling	138
6.4	Laser cooling in 2D perovskite single crystal	140
6.4.1	Laser cooling results	140
6.4.2	Cooling of a thermal load on perovskite crystal	141
6.5	Discussion	143
6.6	Summary	145
Chapter 7: Conclusions and future works		146
7.1	Conclusions	146
7.2	Future works.....	149
References		156
Publication list		169

List of abbreviations

0D: zero dimensional
1D: one dimensional
2D: two dimensional
3D: three dimensional
ASE: amplified spontaneous emission
ASPL: anti-Stokes photoluminescence
CB: chlorobenzene
CBM: conduction band minimum
CCD: charge coupled detector
CVD: chemical vapor deposition
DBR: distributed Bragg reflector
DCM: dichloromethane
DMF: dimethylformamide
FET: Field effect transistor
FWHM: full width half maximum
HOMO: highest occupied molecular orbital
IR: infrared
LED: Light emitting diode
LUMO: lowest unoccupied molecular orbital
MA: methylammonium
NP: nanoparticle
OA: oleic acid
PCBM: phenyl-C61-butyric acid methyl ester
PL: photoluminescence
PLQY: PL quantum yield
PVD: physical vapor deposition
RT: room temperature
TMD: transition metal dichalcogenide
UV: ultra violet
VLS: vapor-liquid-solid
VBM: valence band maximum
VIS: visible
XRD: X-ray diffraction
WGM: whispering-gallery mode

Citations to published work

Majority of Chapter 1 appears in:

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Majority of Chapter 5 appears in:

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“Whispering Gallery Mode Lasing from Layered Materials”. Xinfeng Liu, **Son Tung Ha**^{*}, Qing Zhang, Tze Chien Sum^{*}, Qihua Xiong^{*}, *ACS Nano*. 9(1), 687-695 (2015). **as co-first authors*

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“Laser Cooling of Organic-inorganic Lead Halide Perovskites”. **Son-Tung Ha**, Chao Shen, Jun Zhang, Qihua Xiong, *Nat. Photonics*, 10, 115-121 (2016).

Chapter 1 : Introduction

1.1 Perovskite materials

Recently, metal halide perovskites have received substantial attention from research community due to a number of their applications in solar cells¹⁻³, lasers⁴⁻⁶, light emitting diodes (LED)⁷⁻⁹, water splitting^{10,11}, laser cooling¹² *etc.* The material is now considered as the most promising material for the future of opto-electronics because of its high performance, low cost, and abundance¹³. Lead halide perovskites was firstly used in dye-sensitized solar cell configuration in 2009 by Miyasaka and colleges with an initial efficiency of only 3.8%.¹⁴ Since then, the performance of perovskite solar cell has been dramatically improved mostly by material and interface engineering which boosted the efficiency over 20%.¹⁵ The perovskite material exhibits excellent optical and electrical properties being high absorption coefficient, strong photoluminescence, low trap-state density, and long charge diffusion length.^{4,16-18}

The term “perovskite” was originated from calcium titanate (CaTiO_3) crystal structure, which was named in honor of the Russian mineralogist Lev Perovski.¹⁹ Historically, organic-inorganic perovskites with the general formula $[(\text{R-NH}_3)_2\text{MX}_4]$ were first synthesized by Remy and Laves in 1933.²⁰ They synthesized a series of copper perovskites containing chloride and short alkyl amino group. Later, lead and tin based perovskite with formula MAPbX_3 ($\text{MA} = \text{CH}_3\text{NH}_3$, $\text{X} = \text{Cl}$, Br , and I) and $\text{MASnBr}_x\text{I}_{3-x}$ were synthesized and characterized by D. Weber in early 1980s.^{21,22} The first study of electrical properties for tin-based perovskite was reported by Mitzi *et al.* in 1994 as a new family of semiconductor materials.²³ After that, the perovskites have been used in various forms of devices such as field effect transistor (FET), LED with limited performance.²⁴⁻²⁶ However, their physical and chemical properties had not been

thoroughly investigated with a sufficient research effort due to the lack of potential applications at that time.²⁷ The attention for this material was only raised up again when it was applied in solar cell in 2009¹⁴ which later turned out to be one of the most effective light absorber material for solar cell to date.

Figure 1-1: Structure of 3D and 2D perovskites: a) Structure of AMX₃ 3D perovskite; b) Structure of layered perovskites with (left) monoammonium (RNH₃⁺) or (right) diammonium (⁺H₃N-R-NH₃⁺) organic cations.

Metal halide perovskites are mainly classified into two categories based on their crystal structure motif. The first one is called 3D-structured perovskite with the general chemical formula AMX₃ and the other is called 2D-structured or layered perovskite with the formula A₂MX₄ where M is divalent metal such as Pb, Sn; X is a halide (Cl, Br, or I); and A is a cation which can be inorganic (*e.g.* Cs⁺) or organic (*e.g.* CH₃NH₃⁺, C₄H₉NH₃⁺, C₆H₅-C₂H₄NH₂⁺, *etc.*). We should not be confused by the term 3D and 2D here which are related to the structural motifs of the material while the other 0D - 3D refer to the dimension of materials. In the perovskite structure, the divalent metal M is surrounded by six halogen atoms in an octahedron structure, and the cation A is either located in the center of eight MX₆ octahedral network (in the case of 3D perovskite) or sandwiched between corner-sharing MX₆ octahedral layers (in 2D perovskite) as illustrated in Figure 1-1.

The crystalline structure of perovskites (AMX₃) in its cubic structure (α -phase) has a unit cell of five atoms, in which the cation A is surrounded by twelve anion X while

the cation M is surrounded by six as shown in Figure 1-2a. In order for this structure to be stable in ideal cubic phase, the tolerance factor t – a function of ionic radii of A, M and X site ions- should be close to 1.

$$t = \frac{(R_A + R_X)}{\{\sqrt{2}(R_M + R_X)\}} \quad (1-1)$$

where R_A , R_M , and R_X are the ionic radii of the corresponding ions. If the tolerance factor is far from this ideal value, then the symmetry of the crystalline structure would be lowered. From the formula (1-1) we can see that the radii of cation A must be much larger than that of cation M in order to satisfy the ideal cubic condition (*i.e.*, tolerance factor = 1). In the scope of interest, M is usually lead (Pb) or tin (Sn) which are very big atoms. Thus, the cation A must be extremely large.

Figure 1-2. (a) Crystalline structure of cubic (α phase); (b) crystalline structure of the tetragonal crystal system (β) phase and orthorhombic (γ) phase of MAPbX₃; and (c) the tolerance factor for different perovskite material systems, $t = 1$ is ideal. Image: (a) Copyright Ref.²⁸; (b) Copyright Ref.²⁹; and (c) Copyrights from Ref.³⁰

The crystalline structure of perovskite could remain cubic if the tolerance factor lies between $0.89 - 1$.³¹ Below this range, the perovskite will have lower symmetry crystalline structure such as tetragonal (β -phase) or orthorhombic (γ -phase). On the contrary, when the tolerance factor is larger than 1 (*e.g.*, when A is a long chain amino), it would undermine the 3D M-X network, leading to layered structure perovskite as shown in Figure 1-1b. The perovskite material can undergo phase transition at different temperature. MAPbI₃ (tolerance factor = 0.83), for instance, has orthorhombic phase at low temperature (*i.e.*, <150K), tetragonal phase at medium temperature (*i.e.*, 150 – 340K), and cubic phase at higher temperature (*i.e.*, >340 K). This phase transition would affect the thermal stability and performance of perovskite devices. Perovskite with tolerance factor lying closer to the ideal range (*i.e.*, $0.89 - 1$) would have higher stability as in the case of FAPbI₃ (tolerance factor = 0.88).

1.2 Synthesis of low dimensional perovskite single crystals

Metal halide perovskites represent a vast family of interesting semiconducting material with exceptional optical and electronic properties. Unlike traditional III-V or II-VI semiconductors, there are thousands of combinations for the perovskite composition that can be easily synthesized. By changing the perovskite composition, it is able to tune the characteristics of the material such as band-gap, conductivity, mobility, and so forth, which are very important for device configuration and optimization. The abundance of material, low cost, and high performance of perovskite make this family of materials a high position in the map of future optoelectronic applications. Many other efforts have been made to prepare and characterize low dimensional forms of the perovskites.³²⁻³⁵ In our group, nanoplatelets and nanowires of perovskites have been prepared by vapor phase synthesis to realize their excellent

natural cavity in optical lasing.^{5,36-38} The high crystallinity and optical quality of the nanoplatelets also enabled the experimental demonstration of laser cooling in the perovskite material.¹² The high external quantum efficiency of colloidal quantum dots of perovskites further boosted their performance in light emitting diode.^{8,39} Recently, the idea of hetero-structuring perovskite 2D sheet and other 2D materials such as graphene or transition metal dichalcogenide becomes an interesting concept for integrating this material to low dimensional optoelectronics.

1.2.1 Perovskite quantum dot

The organic-inorganic perovskite colloidal nanoparticles (NPs) was firstly synthesized by Pérez-Prieto *et al.*⁴⁰ The NPs were prepared by a simple and reliable method under ambient atmosphere, in which a dimethylformamide (DMF) solution of $\text{CH}_3\text{NH}_3\text{Br}$ and PbBr_2 reacted and precipitated in the acetone solution in the presence of long chain alkyl ammonium bromide, oleic acid (OA) and octadecene. They proposed the growth mechanism as while the methylammonium (MA) cations are embedded in the voids of the corner-sharing PbX_6 octahedra, the long alkyl chain cations only fit the periphery of the octahedra with their chains dangling outside it. Thus, these ammonium ions would act as the capping ligands to limit the growth of the colloidal NPs extending in three dimensions. The XRD patterns showed a cubic phase of the MAPbBr_3 NPs and the HRTEM images showed the spherical morphology of the NPs with an average size of 6 nm. The MAPbBr_3 colloidal NPs exhibited an absorption peak at 525 nm and a PL peak at 527 nm which is blue-shifted compared to the absorption peak at 550 nm and PL peak at 570 nm of MAPbBr_3 bulk crystal. The colloidal NPs showed a high PL quantum yield (PLQY) of 20% in toluene and can be kept stable in series of aprotic, moderate polarity, organic solvents for more than three months. Next, they further optimized the synthesis of MAPbBr_3 colloidal NPs by tuning

the ratio of MABr, PbBr, OABr and octadecene.⁴¹ Finally, the best colloidal NPs with particles size of 5.5 nm and PLQY of 83% were obtained by using lager ratio of the ammonium and PbBr₂ but in the absence of oleyamine.

A similar precipitation method was also used to synthesize the mixed halide perovskite MAPbX₃ colloidal NPs with different Br/I and Br/Cl composition (Figure 1-3).⁴² The PL spectra of these mixed halide perovskite can be finely tuned from 407 to 734 nm by varying the composition of halogen cations and their absolute PLQYs can be reach 50 – 70%. Typically, MAPbBr₃ NPs have an average diameter of 3.3 nm and PLQY of 70%. The exciton binding energy of MAPbBr₃ NPs was calculated to be 375 meV, which is much larger than that of the bulk counterpart of 65 meV. Rogach *et al.* reported a synthesis of MAPbBr₃ NPs in the variation of the temperature of the poor solvent between 0-60 °C.⁴³ The MAPbBr₃ NPs size can be controlled by the temperature; 1.8 nm, 2.8 nm, and 3.6 nm average diameters were obtained under 0, 30, and 60 °C. The PL spectra were tuned from 470 nm (0 °C) to 520 nm (60 °C) and the PLQYs of the series colloidal NPs started at 74% for the 0 °C sample and steadily increased, reaching as high as 93% for the 60 °C sample. However, these results are still not enough to confirm the quantum confinement of the perovskite colloidal NPs. That is because the long chain alkyl ammonium was used as ligands to synthesize the perovskite NPs, which might form quasi-2D perovskite with blueshift PL spectra.^{44,45} Our group also reported the synthesis of the perovskite MAPbX₃ colloidal NPs with emission from 403 to 740 nm.⁸ But we used the different precursor solution; the DMF and γ -butyrolactone as the solvent, oleic acid as ligands and without oleyamine. Here, the absence of the oleyamine can keep the colloidal solution more stable, even storing for several months. It can be deduced from the XRD patters and HRTEM that the as-synthesized perovskite colloidal NPs exhibit a typical amorphous phase, which is

attributed to free PbX_6 ($X = \text{Br}$ or DMF anion) dispersed in the DMF and γ -butyrolactone mixed solution. When the precursor solution was injected in toluene, PbX_6 units would aggregate and re-precipitate, but the crystallization process would be blocked by the oleic acid. Notably, the HRTEM was conducted at low acceleration voltage of 60 kV to exclude the possible recrystallization of the amorphous perovskite under high acceleration voltage. Although the re-precipitation method is a fast and facile strategy to synthesize a high luminescent MAPbX_3 colloidal NPs, the yield of the product is very limited due to the formation of aggregated NPs together with the NPs.

Figure 1-3. (a) Schematic illustration of the reaction system and process for LARP technique and typical optical image of colloidal MAPbBr_3 solution. (b) HRTEM image of MAPbBr_3 colloidal NPs. (c) Optical absorption and PL spectra of perovskites with different halides component. (d) Digital image of perovskite colloidal solutions in toluene under ambient light and UV lamp, light emission from 438 to 660 nm. Copyrights from Ref.^{8,42}

The high PLQY of perovskite MAPbX₃ colloidal NPs motivated the preparation of inorganic CsPbX₃ (X = Cl, Br, I, and mixed Cl/Br and Br/I) NPs. Kovalenko *et al.* firstly synthesized CsPbX₃ colloidal NPs by injecting the precursors Cs-oleate into PbX₂ solution containing oleyamine, oleic acid, trioctylphosphine, and octadecene at high temperature as in the case of CdS/Se quantum dots.⁴⁶ The CsPbX₃ colloidal NPs exhibit cubic shape (4–15 nm edge lengths) and cubic perovskite crystalline structure. Through compositional modulations and quantum size-effects, the emission spectra are also tunable over the entire visible spectral region of 410–700 nm. PL of CsPbX₃ NCs shows narrow emission line widths of 12–42 nm (from blue to red) and high PLQY of 50–90%. Within the effective mass approximation, they have estimated the effective Bohr diameters of Wannier–Mott excitons and the binding energies for CsPbCl₃ (5 nm, 75 meV), CsPbBr₃ (7 nm, 40 meV), and CsPbI₃ (12 nm, 20 meV). Kovalenko and Manna *et al.* further observed the fast anion exchange in CsPbX₃ (X = Cl, Br, I) perovskite NPs at low temperature.⁴⁷ By adjusting the halide ratios in the colloidal nanocrystal solution, the bright PL could be tuned over 410–700 nm while maintaining high quantum yields of 20–80% and narrow emission line widths of 10–40 nm. Furthermore, the fast inter-nanocrystal anion-exchange was also demonstrated between the CsPbCl₃, CsPbBr₃, and CsPbI₃ NPs, leading to uniform CsPb(Cl/Br)₃ or CsPb(Br/I)₃ compositions. After that, there are many reports on the CsPbX₃ colloidal NPs synthesized based on this methods, but with different crystal phase. For example, Nag *et al.* synthesized CsPbBr₃ colloidal NPs following above methods, but obtain orthorhombic phase of CsPbBr₃.⁴⁸ It should be noted that the colloidal NPs with

broaden XRD peaks and the cubic and orthorhombic phase feature very closed XRD patterns, so it is difficult to distinguish these phases.

Figure 1-4. Transmission electron microscopy (TEM) images of ~ 10 nm CsPbX₃ NCs after treatment with various quantities of (a) chloride and (b) iodide anions. The insets show the evolution of emission colors under UV lamp. Copyrights from Ref.⁴⁷

Inspired by the methodology for synthesis of perovskite MAPbX₃ colloidal NPs, Zeng *et al.* extended the supersaturated recrystallization method into inorganic perovskite CsPbX₃.⁴⁹ Although crystallized at RT, these colloidal NPs have superior optical properties as those formed at high temperature, including PLQYs of 80%, 95%, and 70% for red, green, and blue PLs, and 90% retention rate after aging 30 d in ambient conditions. Deng *et al.* used a reprecipitation strategy for systematically manipulating the shape of CsPbX₃ colloidal NPs, such as spherical colloidal NPs and nanocubes, by using different ligands.⁵⁰

Hens *et al.* studied the dynamic ligand of the inorganic perovskite CsPbX₃.⁵¹ They found that compared to the classical chalcogenide quantum dots, CsPbX₃ are more ionic in nature and the interactions with capping ligands are also more ionic and labile.

Therefore, ligand binding to the NPs surface is highly dynamic and easily lost during the isolation and purification procedures. However, when a small amount of both oleic acid and oleylamine is added, the NPs can be purified, maintaining optical, colloidal, and material integrity. A high amine content in the ligand shell would increase the quantum yield due to the improved binding of the carboxylic acid.

1.2.2 Perovskite nanowires

As lead halide perovskites have triggered a revolution in the photovoltaic solar cells, much efforts have been spared on the synthesis of large area lead halide perovskite films for their excellent optoelectronic properties.^{2,7,52-57} Nonetheless, one dimensional lead halide perovskite nanowires are also of great importance for their novel optical and electronic properties, as well as the potential building blocks for various applications in optoelectronic devices.^{6,36,58-61} Over the past decades, a lot of efforts have been spent on the synthesis of II-VI and III-V semiconductor nanowires, which is mainly based on a chemical vapor deposition (CVD) process.⁶²⁻⁶⁶ This approach is the most widely used due to its versatility and simplicity in many semiconductor systems. The CVD process to obtain nanowires primarily based on a vapor-liquid-solid (VLS) mechanism, utilizing noble metal films as the catalyst to drive the one dimensional crystal growth. However, this VLS method is rarely adopted in the growth of perovskite nanowires, which could be possibly attributed to the low growth temperature of perovskites.

Compared with previous III-VI and II-VI semiconductors based on a VLS mechanism, facile solution processed synthesis of lead halide perovskite could be the most attractive point for low cost applications.^{4,17,67-69} Much efforts have been devoted to synthesizing lead halide perovskite nanowires by solution methods.^{61,70-72} Large area high quality single crystal methylammonium (MA) lead halide perovskite nanowires

were reported in the pioneering work on the nanowire laser by Zhu *et al.* and his co-workers.⁷¹ In this work, no surfactant ligand is used for the controlled anisotropic crystal growth. A lead acetate (PbAc_2) solid thin film firstly was deposited on glass substrate by using 100 mg ml^{-1} $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ aqueous solution. This PbAc_2 solid film was then immersed in the $\text{CH}_3\text{NH}_3\text{X}$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$ or mix halide precursors) solution in isopropanol in an ambient environment for over ~ 20 h. Consequently, high quality methylammonium lead halide perovskite nanowires were obtained with lengths up to $20 \text{ }\mu\text{m}$ and flat rectangular end facets (Figure 1-5b). The width of the rectangular end facets is typically a few hundred nanometers. The corresponding X-ray power diffraction pattern (Figure 1-5c) confirms the pure tetragonal phase of single-crystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanowire, the cubic phase of single-crystalline $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and single-crystalline $\text{CH}_3\text{NH}_3\text{PbCl}_3$ nanowires. A dissolution-recrystallization growth mechanism was proposed in the above growth procedure. $\text{CH}_3\text{NH}_3\text{PbX}_3$ thin film immediately forms at the surface, which severely suppresses the diffusion of CH_3NH_3^+ ions. This results in a large amount of PbAc_2 remaining on the substrate and slowly dissolving into the solution until PbX_4^{2-} reaches the equilibrium point for precipitation with CH_3NH_3^+ and further reaches the supersaturation to crystallize into $\text{CH}_3\text{NH}_3\text{PbX}_3$. Consequently, a low precursor concentration (and thus supersaturation) was maintained for the anisotropic one-dimensional crystal growth of $\text{CH}_3\text{NH}_3\text{PbX}_3$.^{71,73}

Figure 1-5. (a) and (b) SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanostructures. (c) PXRD patterns of as-grown $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) NWs. (d) TEM images of CsPbX_3 NWs with various degrees of conversion with chloride and iodide anions. The insets show the evolution of emission color (UV excitation, $\lambda = 365 \text{ nm}$) upon forming mixed-halide $\text{CsPb}(\text{Br}/\text{Cl})_3$ and $\text{CsPb}(\text{Br}/\text{I})_3$ NWs. HRTEM images of (e) Cl- and (f) I-exchange NWs. Copyrights from Ref.^{71,73}

Followed after this work, a solution processed method with surfactant ligand was reported to control the synthesis of all-inorganic perovskite CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ or mixture of halides) nanowires.⁷⁰ This method is widely used in previous metal and inorganic semiconductor nanowires, using surfactant ligand as the capping ligand to initiate one dimensional crystal growth. The CsPbX_3 nanowires were synthesized under air-free environment by reacting cesium oleate with lead halide in the presence of oleic acid and oleylamine in octadecene at $150 - 250^\circ\text{C}$ for 5-10 mins. Oleylamine here serves as capping ligand of Pb^{2+} , reducing the activity of Pb^{2+} precursor. Meanwhile, oleylamine preferentially bind to certain facets of CsPbX_3 , leading to the anisotropic, one dimensional crystal growth to obtain perovskite nanowires. The as-synthesized

CsPbX₃ perovskite nanowires exhibits diameter less than 12 nm and length up to 5 μ m. However, the production yield of nanowires is not high and a lot of byproducts, such as nanoplates and nanocrystals, are produced along with the nanowires. By replacing the original oleic acid with octylamine, the nanowire yield has been dramatically improved, yielding up to 90% after simple purification.⁷² Moreover, by anion exchange reaction, CsPbCl₃ and CsPbI₃ nanowires can be transformed from CsPbBr₃ nanowires by reacting with other halide precursors, as shown in Figure 1-5d and e. The nanowires transformed from CsPbBr₃ nanowires exhibits high quantum efficiency up to 83% and 30% for CsPbI₃ and CsPbCl₃ nanowires, respectively. As shown in Figure 1-5e and f, single crystalline features of CsPbI₃ and CsPbCl₃ are still maintained after transformations, confirmed by their HRTEM images.⁷² High crystallinity and excellent optical properties enables perovskite nanowires to serve as promising candidates for optoelectronic applications.

In addition to solution phase synthesis of perovskite nanowires, high quality perovskite nanowires has also been obtained through a vapor phase synthesis. Inspired by our previous work on the growth of perovskite nanoplatelets,³⁸ Xing *et al.* reported similar approach to synthesize high crystalline quality methylammonium lead iodide perovskite nanowires.³⁶ Briefly, PbI₂ nanowires firstly were synthesized on silicon dioxide substrate by placing the PbI₂ precursors in a chemical vapor deposition furnace. Figure 1-6a shows the scanning electron microscopy image of PbI₂ nanowires. PbI₂ nanowires were vertically grown on the silicon dioxide substrates and possess rectangular or near square cross section. Those nanowires were subsequently transferred to another substrate by pressing the new substrate on top of the original substrate with vertically grown nanowires, as shown in Figure 1-6b. Consequently, nanowires on the new substrate were placed in the furnace for conversion into

perovskites by intercalating the $\text{CH}_3\text{NH}_3\text{I}$ molecular into the interval sites of PbI_6 octahedrons layers. The nanowire morphology was still maintained before and after conversion. The converted perovskite nanowires exhibit single crystalline property and grow along the $[100]$ direction, which are confirmed by their SAED pattern (Figure 1-6c and d). However, for this kind of two-step method, the reaction needs to be carefully controlled as incomplete reaction will result in the polycrystalline products or dual-existence of perovskite and PbI_2 . With their nanowire morphology as the active resonator, these vapor phased perovskite nanowires exhibits excellent performance as a laser source.

Figure 1-6. (a) SEM image of PbI_2 nanowires grown on silicon substrate. (b) Optical microscopy image of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanowires on silicon substrate. Inset to (b) is the magnified image. (c), (d) TEM and HRTEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanowire. Inset to (c) is its corresponding SAED pattern. Copyright from Ref.³⁶

1.2.3 Perovskite nanoplatelets

Among all low dimensional forms, 2D material is probably the most important one for practical applications in optoelectronic devices. Because its lateral size is at macro-scale, the 2D material can be easily integrated with other existing electronic materials in a scalable way. Stacking different 2D materials in a designable configuration can create sophisticated devices such as FET, photodetector, LED, solar cell which are usually difficult to perform in a single crystal of 0D or 1D material. Nanoplatelets, a quasi-form of 2D material, have lateral size of tens of micrometers and thickness of few to few tens of nanometers. In research, it is usually easier to prepare 2D material in the form of nanoplatelets or nanoflakes rather than millimeter scale film. The fact that nanoplatelet is defect-free, high quality single crystal, and having large lateral size enough for any optical or electronic characterizations makes it preferable to be subjected for 2D material study. The 2D perovskite is no exception. We reported the synthesis of lead halide perovskite nanoplatelets using a home-built vapor deposition system as illustrated in Figure 1-7.³⁸ In this two-step method, first lead halide crystals are grown on muscovite mica substrate utilizing Van de Waals epitaxial growth mechanism (Figure 1-7a). The super smooth surface of freshly cleaved mica and low mismatch ratio between lead halide lattice constants and those of mica endures the horizontal growth of the crystals which results in nanoplatelet form. The as-grown lead halide nanoplatelets were then intercalated with methylammonium halide using the same vapor deposition system which converted the nanoplatelets into respective perovskites (Figure 1-7b). After conversion, the perovskite nanoplatelets thickness was increased by the factor of ~ 1.8 while remaining lateral dimensions comparable to their PbI_2 counterparts (Figure 1-7c) in good agreement with theoretical calculation based on the crystalline structures of the two compounds. The resulted perovskite nanoplatelets were shown to have excellent optical properties and high crystallinity.

The $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet was shown to have twice electron diffusion length as that of solution processed film. The synthesis and properties of these perovskite platelets will be discussed more in detail in Chapter 3 and Chapter 4 of this thesis.

Figure 1-7. Morphological characterizations of lead halides nano-platelets as-grown on muscovite mica substrate: a) Optical (above) and SEM (below) images of lead halides: A,D: PbCl_2 ; B,E: PbBr_2 ; C,F: PbI_2 . b) Schematic of the synthesis setup using a home-built vapor-transport system. c) Thickness of PbI_2 platelets before (images above data line) and after being converted to $\text{CH}_3\text{NH}_3\text{PbI}_3$ (images below data line). d) Optical properties of different lead halide perovskites ($\text{CH}_3\text{NH}_3\text{PbX}_3$). Copyrights from Ref.³⁸.

Liu *et al.*⁷⁴ introduced a different approach using hot casting aqueous solution of PbI_2 on SiO_2 substrate to form PbI_2 nanoplatelets and then converting to perovskite by intercalating methylammonium halide using a vapor deposition system. Due to the layered structure nature of PbI_2 , the crystals tend to self-assemble into platelet form in

its aqueous solution during hot casting process. Thanks to its layered structure, the PbI_2 nanoplatelets can also be prepared by mechanical exfoliation from its bulk crystal as reported by Cheng *et al.*⁷⁵ The common between the three methods above is that they are all two-step method in which a physical growth of lead halide nanoplatelets is followed by a vapor phase intercalation of methylammonium halide. These approaches, especially the first one – using vapor deposition system for all steps, have an advantage of using high purity sources of precursors and eliminating the possible contamination and by-product during synthesis. However, due to the two-step growth and the solid phase intercalation of lead halide, the crystallinity of resulted perovskite nanoplatelets may not be as good as in single crystal growth in solution phase.

Wang *et al.* reported a simple method to grow single crystal perovskite microplates.⁷⁶ Perovskite in *N,N*-dimethylformamide (DMF) solution was drop-casted onto a hydrophobic substrate (*i.e.* ITO scribed with polyethylene film). The formation of self-assembly microplates was controlled by the volume ratio of perovskite solution and an anti-solvent – dichloromethane (DCM). The dispersion of DCM vapor in perovskite solution induced the nucleation and subsequent growth of perovskite microplates. The above methods were applied for 3D-structured perovskites where the thickness of nanoplatelets was in order of tens or even hundreds of nanometers. The nature 3D crystalline structure of these perovskites makes them difficult to be prepared at mono- or even few layers thick. The other type of perovskite, which has 2D layered structure, may be a better candidate to study in the 2D form. Indeed, Dou *et al.*⁷⁷ reported a solution method to prepare monolayer square sheets of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ which opened up a new direction to study perovskite at atomically thin level comparable with other 2D materials such as graphene or TMD. The result is summarized in Figure 1-8 below.

Figure 1-8. Synthesis of atomically thin 2D $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ crystals. (A) Structural illustration of a single layer $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ (blue balls, lead atoms; large orange balls, bromine atoms; red balls, nitrogen atoms; small orange balls, carbon atoms; H atoms were removed for clarity). (B) Optical image of the 2D square sheets. Scale bar, 10 nm. (C) AFM image and height profile of several single layers. The thickness is around 1.6 nm (± 0.2 nm). (D) AFM image and height profile of a double layer. The thickness is around 3.4 nm (± 0.2 nm). Copyrights from Ref.⁷⁷

In this method, a diluted solution of perovskite in co-solvent system of chlorobenzene (CB), acetonitrile and DMF was dropped onto Si/SiO₂ substrate prior to mild heating of the substrate to induce crystal growth of the perovskite square sheets. The co-solvent system played an important role as CB and acetonitrile help to reduce

the solubility of perovskite in DMF and promote the crystallization. The diluted solution of perovskite (*i.e.* 10^{-3}M) was also critical to obtain monolayer sheets.

One of the common methods to prepare nanoplatelets in the literatures is to use a surfactant as morphology assisted agent during the growth of a material in solution. Despite the fact that using surfactant will introduce contamination onto the surface of the grown materials and may eventually reduce their performance in electronic properties, this is one of the few methods that provide highest throughput and reproducibility. Song *et al.*⁷⁸ and Sun *et al.*⁵⁰ both applied similar approach to synthesize nanoplatelets of cesium lead bromide perovskite (CsPbBr_3). Both method used long-chain alkyl amines such as oleyl amine, dodecylamine, octylamine, and long-chain carboxylic acids such as oleic acid as co-surfactants. Instead of using cesium halide as precursor like other method, they used carboxylates of cesium such as cesium oleate or cesium stearate for better solubility in hydrocarbon solvent which was the medium for the reaction. The result is that they can synthesize a large scale of nanoplatelets with high monodispersity and control the thickness of the perovskite down to monolayer as shown in Figure 1-9 below.⁷⁸

Figure 1-9. Synthesis of 2D ultrathin CsPbBr_3 nanoplatelets: a) Low-magnification and b) high-magnification SEM images. c,d) AFM image and height profile of a monolayer (c) and bilayer (d) CsPbBr_3 nanoplatelets with a thickness of 1.6 and 3.3 ± 0.2 nm, respectively. e) Thickness distribution histograms for CsPbBr_3 nanoplatelets prepared through solution-phase synthesis. Copyrights from Ref.⁷⁸

1.3 Optical properties of perovskite nanocrystals

1.3.1 Band structure of perovskite

The band structure of metal halide perovskite is predominantly determined by the MX_6 building block. In lead based perovskite, for instance, the valence band (or highest occupied molecular orbital, HOMO) is mainly contributed by Pb 6s- I 5p σ -antibonding orbitals while the conduction band (or lowest unoccupied molecular orbital, LUMO) is from the Pb 6p- I 5p π -antibonding and Pb 6p- I 5s σ -antibonding orbitals.³¹ The

electronic performance of perovskite can be attributed to the lone pair of s electrons in Pb cation. In contrast to most metal cation whose most outer s orbitals are empty, Pb has an occupied $6s$ orbital lying below the valence bands.^{28,79} The valence band maximum (VBM) has strong antibonding character of Pb- $6s$ and I- $5p$, while the conduction band minimum (CBM) is mainly contributed from Pb $5p$ state. These unique characteristics of the perovskite is attributed to its dual nature of electronic structures being both ionic and covalent characteristics. Figure 1-10a shows the contribution of each component on the density state of MAPbI₃ perovskite and its schematic optical absorption (b) in comparison with other solar cell absorber: Si (c) and GaAs (d).

Figure 1-10. Electronic band structure of perovskite. (a) Contributions of MA, Pb, and I on the density of state of MAPbI₃ perovskite. The schematic optical absorption of: perovskite (b); Silicon (c); and GaAs (d). Copyrights from Ref.³¹

In conventional semiconductor such as GaAs, VBM is mostly contributed by As- p orbital and the CBM is contributed by Ga- s orbital. On the contrary, perovskite exhibits an opposite electronic band structure as shown in Figure 1-10b, d. The electronic band structure of perovskite is also responsible for its strong optical absorption property comparing to that of other solar cell absorbers. The absorption coefficient in the visible range of CH₃NH₃PbI₃ is 1-order of magnitude higher than that of GaAs and about 2-orders of magnitude higher than that of silicon.⁸⁰ This property is

particularly helpful for solar cell and opto-electronic device applications since less material is needed for optimal absorption of solar spectrum. Several other excellent electronic properties such as: efficient charge transport, high carrier mobility, and long carrier diffusion length can also be attributed to the unusual electronic band structure of perovskite.⁸⁰⁻⁸²

1.3.2 Bandgap tunability

As perovskites have triggered a revolution in the solar cell research field, they have attracted a lot of attention in the past few years thanks to their excellent exciton and carrier properties. Apart from their superior performance in the solar cell research area, perovskite themselves also serve as outstanding light emitters in the LED, laser applications.^{5,9,39,83-89} Compared with conventional III-V and II-VI semiconductors, one of the most attracting points in perovskites is facile tunable emission throughout the whole visible range by controllable stoichiometry. The emission of perovskite can be tuned by substituting halide elements from chloride to iodide. By substituting either mixture of chlorides and bromides, or bromides and iodides, the emission of all inorganic-perovskite CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$, or their mixture), including quantum dots and nanoplatelets, can be well tuned from 400 nm (blue) to 700 nm (red), which covers the whole visible region as shown in Figure 1-11.^{37,42,46} Another way to tune the emission is to replace the lead with other kinds of metal ions, or insert other kinds of organic molecules. The emission of perovskite can be further tuned to near infrared or ultraviolet region.^{59,84}

Figure 1-11. (a) Colloidal perovskite CsPbX₃ NCs (X = Cl, Br, I) solutions in toluene under UV lamp ($\lambda = 365$ nm); (b) representative PL spectra ($\lambda_{\text{exc}} = 400$ nm for all but 350 nm for CsPbCl₃ nanocrystals). (c) Optical absorption and PL spectra of CsPbCl₃, CsPbBr₃, and CsPbI₃ nanoplatelets. Inset: PL image of CsPbCl₃, CsPbBr₃, and CsPbI₃ nanoplatelets. Copyrights from Ref.^{37,42,46}

1.3.3 Photoluminescence quantum efficiency

Quantum efficiency, defined as the ratio of the number of converted photon to absorbed photon, is one of the most crucial properties for applications involving optical gain. High quantum efficiency usually signifies that most of the absorbed photons were converted through radiative recombination processes rather than non-radiative recombination processes. Perovskites are regarded as excellent light emitters for their large absorption coefficient and high quantum efficiency.⁴⁷ High quantum efficiency up to 90% has been reported in both all-inorganic CsPbX₃ and organic-inorganic methylammonium lead halide perovskite nanocrystals without any further surface treatment.^{90,91} While in conventional III-V and II-VI semiconductors, their nanocrystals usually suffer from surface defect states or donor-acceptor levels which strikingly reduces the quantum efficiency. The high quantum efficiency in perovskite is the result of clear bandgap with negligible charge-trapping states, which greatly promote the

exciton radiative recombination efficiency.⁹² With the high quantum efficiency, perovskites are promising alternatives for many optoelectronic applications including lasing, light emitting diode, *etc.*

1.3.4 Quantum confinement effect

When the size of a semiconductor is too small to be comparable to Bohr radius of excitons, quantum confinement could be observed on the optical properties of the semiconductor. Excitons are confined in all three spatial dimensions, which results in a transition from continuous to discrete energy levels. Consequently, the optical absorption and emission properties could be tuned by changing the size of the semiconductor. Quantum confinement effect are usually associated with nanocrystals and result in the blue shift of bandgap with the decrease of the size. In all-inorganic CsPbBr₃ perovskite nanocrystals, the exciton Bohr radius is calculated to be 7 nm, quantum confinement effect is quite prominent in CsPbBr₃ perovskite nanocrystals when its size becomes comparable with the exciton Bohr radius. The emission of CsPbBr₃ perovskite nanocrystals can be truly tuned from around 2.7 eV to 2.4 eV with the size changing from 4 nm to 12 nm which is in good agreement with theoretical calculation as shown in Figure 1-12a and b.⁴⁶ Similarly, quantum confinement effect is also observed in organic-inorganic methylammonium lead halide perovskite nanocrystals.⁹¹ Quantum confinement effect opens a way to tune the emission of semiconductors, which provides the potential in various light emitting applications.

Figure 1-12 (a) Quantum-size effects in the absorption and emission spectra of 5–12 nm CsPbBr₃ NCs. (b) Experimental versus theoretical (effective mass approximation, EMA) size dependence of the band gap energy. Copyrights from Ref. ⁴⁶

1.4 Applications of perovskite beyond solar cell

1.4.1 Optically pumped lasing in perovskite

Metal halide perovskite is well-known for its high absorption coefficient and strong photoluminescence. When a high gain material is put in a suitable optical cavity, one can expect the lasing happens. Since the discovery of amplified spontaneous emission (ASE) in perovskite,⁴ many researches have been done to explore their potential applications in laser technology. Deschler F. *et al.* was among the first to use perovskite as gain medium to achieve lasing by spin-coating the material on top of a distributed Bragg reflector (DBR).⁵³ The other approach is to use perovskite crystal as a natural formed cavity. Our group was among the first to demonstrate that perovskite

nanoplatelets can act as a whispering-gallery mode (WGM) cavity and achieved lasing without the help of artificial optical cavity (Figure 1-13a).⁵ We also demonstrated that high crystalline perovskite nanowires can act as Fabry-Pérot cavity to achieve lasing in the material.³⁶ It is of interesting due to their potential applications in nanoscale optoelectronics. By manipulating the halide content in the perovskite composition, it is possible to precisely control the emission wavelength and achieve lasing in all visible spectrum (Figure 1-13c and d).³⁷ Many other researchers reported similar observation in nanoplatelets and nanowires with high quality factor and low lasing threshold.

Figure 1-13. Optical lasing in lead halide perovskite nanoplatelets and nanowires. (a) Whisper gallery mode lasing in perovskite nanoplatelet cavity. (b) Fabry-Pérot lasing in perovskite nanowire cavity. (c) Optical absorption and photoluminescence of CsPbX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) nanoplatelets. (d) Wavelength tunability of perovskite lasing by changing the composition of halide in CsPbX_3 perovskite. Copyrights from Ref. ^{5,6,37}

Zhu *et al.* demonstrated the lasing in $\text{CH}_3\text{NH}_3\text{PbX}_3$ with exceptionally low threshold of only 220 nJ cm^{-2} (Figure 1-13b) corresponding to a carrier density as low as $1.5 \times 10^{16} \text{ cm}^{-3}$. Another remarkable thing about the nanowires is that it has very low carrier trapping sites and the estimated lasing quantum yield is close to 100%.⁶ We believe that in addition to high optical gain, the high quality crystalline structure of 1D and 2D perovskites is responsible for its high performance as self-lasing material. With their exceptional coherent light emission and the ambipolar charge transport properties, the perovskite materials may someday be applied in electrically driven lasing.

1.4.2 Light emitting diode

Beside the widely-used application in solar cell, metal halide perovskite is emerging as one of the most promising material for light emitting diode due to its easy-to-prepare, low cost, and high performance. One important advantage of perovskites in LED application is that they usually have high color purity with the full width half maximum of $\sim 15\text{-}25 \text{ nm}$ for the electroluminescence spectra. Another advantage is the color tunability in the whole visible spectrum by simply changing the composition of different halides within the compounds. For the LED application, smaller grain size is preferable because it limits the exciton diffusion which in turn increases the possibility for radiative recombination. Thus, quantum dot seems to be a good candidate due to its strong luminescence and high external quantum yield. Indeed, many researchers have reported the use of perovskite quantum dot as active material for LEDs and achieved exceptional performance comparing to solution-prepared film. Our group also prepared amorphous quantum dots of perovskite with some novel properties and used to fabricate LED with performance being among the highest devices to date (Figure 1-14a).⁸ All inorganic perovskites (*i.e.* CsPbX_3) were also synthesized in the form of quantum dots for LED application (Figure 1-14b)⁹³ to overcome the stability issues in organic-

inorganic hybrid perovskite. Even though the performance in LED is lower than quantum dot, perovskite nanoplatelets have also been used to fabricate LED (Figure 1-14c).⁹⁴ The octylamine capped perovskite nanoplatelets showed improvement in device stability and even allowed it to be fabricated in air. All of these achievements make perovskite a new generation of LED material for lighting and display application.

Figure 1-14. Low dimensional perovskite in LED applications. (a) LED from CH₃NH₃PbX₃ quantum dots. (b) LED from CsPbX₃ quantum dots. (c) LED from CH₃NH₃PbX₃ nanoplatelets. Copyrights from Ref. ^{8, 93, 94}

1.4.3 Other applications

Low dimensional perovskites are being tackled in many other optoelectronic applications such as FET, photodetector, and single photon emitter. Liu *et al.*⁷⁴ used

perovskite nanoplatelets to fabricate a FET on Si/SiO₂ substrate. The I - V curve resulted from that device showed a linear dependence on applied bias suggesting ohmic contact between perovskite nanoplatelets and the electrodes. The ratio of photocurrent and dark current can reach up to two orders of magnitude which the authors attributed to strong light mater interaction as well as broad-band light harvesting capacity of the perovskite. Deng *et al.*³² grew and fabricated photodetectors based on horizontal array of CH₃NH₃PbI₃ nanowires on glass substrate. The electrodes were patterned by simple shadow mask with the active channel of 350 μ m. The resulted photodetectors have a response time of 0.3 ms, a responsivity of 1.3 AW⁻¹, and a detectivity of 2.5×10^{12} Jones which are superior to the bulk perovskite and other inorganic nanowire photodetectors. Another interesting application of low dimensional perovskite is the use of 0D quantum dot as a single photon emitter at room temperature reported by Park *et al.*³⁴ The authors used CsPbX₃ perovskite as precursor material to synthesize quantum dots having cubic shapes and an average size of ~ 10 nm. The perovskite quantum dots showed a strong photon anti-bunching of the emitted light and strong photoluminescence (PL) intensity fluctuation correlating with the PL lifetime. They attributed this phenomenon as “A-type blinking” which is commonly observed in quantum dot system.

1.5 Motivation and Objectives of this thesis

Since the first report of using perovskite material in solar cell in 2009, the perovskite has been extensively applied and studied in various optoelectronic devices. While many researchers spent large effort in optimization and improvement of device performance, at the same time, people tried to answer fundamental questions related to the perovskite material itself. Most of the questions are focused on how and why

perovskite performs extremely well in devices such as solar cell and LED. The other questions are what other intrinsic physical properties of this material and what other applications in term of optoelectronics and photonics that the material is good at. In this particular thesis, I will focus on the latter type of questions and try to explore new area of physics and applications beyond solar cell. In order to experimentally study fundamental properties of the material, high quality sample is needed. Thus, the first objective of this thesis is to prepare high purity, single crystal of the perovskites, particularly $\text{CH}_3\text{NH}_3\text{PbX}_3$ (3D structure), $(\text{C}_6\text{H}_5\text{-C}_2\text{H}_4\text{-NH}_2)_2\text{PbI}_4$ (2D structure), and their 2D-3D hybrid structure. The synthesis will be carried by both chemical vapor deposition (CVD) and solution methods.

The second objective of this thesis is to study optical properties of the synthesized perovskite single crystal by various spectroscopy techniques such as: Raman spectroscopy, temperature dependence photoluminescence spectroscopy, time-resolved photoluminescence spectroscopy. From these experiments, several fundamental properties of perovskite will be studied in detail. Temperature dependence photoluminescence spectroscopy will be used to investigate the phase transition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. Time-resolved photoluminescence spectroscopy will be used to determine the carrier diffusion length and exciton dynamic. Raman and photoluminescence spectroscopy will be used to study phonon-assisted upconversion photoluminescence and exciton-electron coupling in both 3D and 2D perovskites. Since most of the application devices and previous fundamental studies on perovskite were done on a solution-processed, polycrystalline, spin-coated film, our study will give more insight into the intrinsic properties of the perovskite material.

Finally, based on the fundamental properties of these single crystal perovskites, several photonic devices will be designed and studied in detail. Two fields of photonics

applications that we are particularly interested in are photonic laser and laser cooling. In this part, we will show that the single crystal perovskite is not only an excellent gain material, but also can serve as a good optical cavity itself. The achievement of lasing at room temperature without the need of an external cavity on our nano/micro scale crystal will be beneficial for integration in nano/micro optoelectronic devices. Another advantage of the perovskite material in the field of laser is its facile tunability of wavelength covering all visible to near IR range. The laser cooling of perovskite presented in this thesis which is a new field of application for the material thanks to its combination of excellent properties: high luminescence quantum yield, low defect density (*i.e.*, low non-radiative recombination, low background absorption), strong phonon-assisted upconverted photoluminescence. The realization of net cooling in perovskite is also attributed to our outstanding sample quality. We will also present the study using our single crystal perovskite as a laser cooling device to cool down a thermal load (CdSe nanobelt).

1.6 Organization of the thesis

Since my objective is to focus on high quality, single crystal perovskite, only synthesis methods and applications of single crystal forms such as quantum dot, nanowires, nanoplatelets will be reviewed. The introduction will be mainly divided into four parts: (1) Crystalline structure of perovskite material; (2) Synthesis of low dimensional perovskite crystals; (3) Optical properties of perovskite crystals; and (4) Application of perovskite single crystal.

In Chapter 2, I will describe the equipment and scientific instruments I used for synthesis (CVD system, solution growth of single crystal) and optical study (Optical

spectroscopy instruments: CRAI20 transmission/reflection micro-spectroscopy, Horiba-JY T64000 micro Raman-spectroscopy, *etc.*) of perovskite in the thesis.

In Chapter 3, I will present the synthesis of single crystal perovskite, both 3D and 2D structures. The synthesis and characterizations of $\text{CH}_3\text{NH}_3\text{PbX}_3$ nanoplatelets, nanowire arrays, and single crystal $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ will be reported. For 2D (layered structure) perovskite, mechanical exfoliation (Scotch-tape based) method will be used to prepare smaller, thinner crystal suitable for optical study.

In Chapter 4, I will present the study on optical properties of single crystal perovskite. In this chapter, the measurement of carrier diffusion length on single $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet using time-resolved photoluminescence spectroscopy will be discussed. In addition, the abnormal bandgap shift and phase transition in the perovskite will also be presented. Finally, the exciton-phonon coupling in layered perovskite single crystal which is responsible for strong upconversion photoluminescence will be discussed.

In Chapter 5, our series works on optically pumped lasing in individual perovskite nanoplatelet will be demonstrated. This chapter consists of three parts. In the first part, I will discuss the observation of lasing in PbI_2 (precursor of lead based perovskite) platelet. In the second part, I will discuss the room temperature near IR lasing on $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet and wavelength tunability in the perovskite family. In the last part, my recent results on lasing in 2D and 2D-3D hybrid perovskites will be presented.

In Chapter 6, I will present the laser cooling results in both 2D and 3D perovskite. Detail of experiment setup, temperature measurement method, and discussion on laser cooling of the material will be presented. In this chapter, the use of 2D perovskite single

crystal as a cooling device to cool down a thermal load (CdSe nanobelt) will also be demonstrated.

Finally, I will conclude my thesis and provide some perspectives of possible future works in Chapter 7.

Chapter 2 : Instrumentation

2.1 Chemical vapor deposition

Chemical vapor deposition (CVD) is a method widely used in semiconductor industry for depositing thin film of various material with very high purity. The difference between CVD and physical vapor deposition (PVD) is that: in CVD, there is a chemical reaction between volatile reactants to form final solid product while in PVD, only physical processes are involved such as evaporation and deposition of sourced materials. In the field of research, both CVD and PVD are widely used to synthesize nanoparticles such as nanobelt, nanowire, and nanoplatelet or thin film of 2D materials such as graphene, transition metal dichalcogenide (TMD). In my experiment, I used a home-built, single zone tube furnace CVD system as illustrated in Figure 2.1.

Figure 2-1. Home-built chemical vapor deposition (CVD) system used in the synthesis of perovskite nanocrystals. Picture of the real system (left) and its simplified diagram (right).

There are three main components in the CVD system. First, the single zone furnace (ThermoFisher Scientific, Lindberg/Blue M TF55035C) with programmable temperature controller is used to heat up the reactants/sources. The maximum temperature in the center of the tube furnace is 1100 °C. The diameter of the quartz

tube is 2.54 cm. The second part of the CVD is a vacuum control system which includes an oil-based high performance mechanical pump connected with a pressure control valve, which modulate the pumping rate controlled by a pressure controller. A capacitive pressure gauge at the upstream (MKS Baratron) provides the actual pressure reading to the pressure controller to compare with the set-point pressure. The minimum base pressure when there is no gas flow can reach around 3 mTorr at room temperature. The last part is a carrier gas/flow rate control unit. This is located at the upstream of the quartz tube. The carrier gas can be chosen from different gas line suppliers including: H₂, O₂, N₂, Ar, Ar/H₂ (5%) for different synthesis requirement. The flow rate of carrier gas can be precisely controlled through a mass flow controller (MKS) with maximum rate of 500 standard cubic centimeter per minute (sccm) for H₂ and 200 sccm for other gases.

In the two-step synthesis of perovskite nanocrystals, the first step is to grow lead halide crystal on muscovite substrate. This step is a PVD process where only physical processes are involved. First, using relatively high temperature (*i.e.*, 300 – 450 °C) and low pressure (50-200 Torr), the source (*i.e.*, PbI₂, PbBr₂, or PbCl₂) which is placed at the center of the quartz tube is evaporated by sublimation. Next, the carrier gas will carry the sublimated source to the downstream of the quartz tube where the substrate is positioned. Finally, the nucleation and growth of crystal on the substrate are induced by the lower temperature at the downstream zone. The second step in the synthesis is to convert lead halide to perovskite by thermally intercalating organic component (*i.e.*, CH₃NH₃X, X= Cl, Br, I) into the pre-grown lead halide crystals. In this step, the organic component will be placed as the source at the center of the quartz tube. The muscovite mica substrate with pre-grown lead halide crystals is placed at the downstream. The hetero-phase chemical reaction will happen at the substrate site between sublimated

gas-phase of $\text{CH}_3\text{NH}_3\text{X}$ and pre-grown PbX_2 crystal. All parameters such as: pressure, gas choice, flow rate, temperature profile, and position of substrate at the downstream will affect to the final crystal morphology and quality.

2.2 Transmission and reflectance micro-spectroscopy

The ultraviolet -visible- near infrared (UV-VIS-NIR) micro-spectrometer is an instrument used to measure spectra of microscopic samples or microscopic area on samples. The spectrometer can be configured to measure transmittance, absorbance, reflectance, polarization, fluorescence, and luminescence spectra of sample areas smaller than a micron. Because of its flexibility, UV-VIS-NIR micro-spectrometers are widely used in many fields of research and industry, especially in the field of nanomaterial research. In this thesis, the CRAIC 20/20 PVTM from Craic Technologies was used to measure transmittance and reflectance of individual single crystal sample as shown in Figure 2-2.

Figure 2-2. UV-visible-NIR micro-spectrometer CRAIC 20/20 PV.

Absorbance spectroscopy is the study of quantized energy transfer between radiation and matter. The energy of light is related directly to its wavelength by the Einstein-Planck relationship:

$$E = h\nu = hc / \lambda \quad (2-1)$$

where E is the energy of the photon, h is the Planck constant ($h = 6.626 \times 10^{-34}$ J.s), ν is the frequency of the photon, c is the speed of light ($c = 3.0 \times 10^8$ m/s), and λ is the wavelength of the photon. The electromagnetic energy of a photon is inversely proportional to its wavelength. Because of the difference in its energy, photons with different wavelengths interact differently with materials. In the UV-visible range, electronic transitions are usually observed in which an electron is excited to higher energy level when a material absorbs a photon. This process is described in an energy level diagram or Jablonski diagram as shown in Figure 2-3. In order to be absorbed by the material, the energy of photon must be exactly equal to the energy difference between ground state and excited state to which the electron is transferred. As shown in the diagram (Figure 2-3), an electron jumps from ground state to first excited state (S1) when a photon with suitable energy is absorbed. Similarly, photon with higher energy absorbed by the material will cause electrons to jump to higher excited state level (e.g., S2, S3).

Figure 2-3. Jablonski energy level diagram illustrating absorbance and fluorescence transition processes.

Reflectance microspectroscopy basically measure the spectra of electromagnetic energy reflected from sample. The portion that is not reflected may have been absorbed by the sample, transmitted through the sample, or even scattered by the sample. There are two types of reflected light: specular and diffusive. Specular reflectance is like the reflectance from a mirror where the light is reflected at the same angle as it impinges on the mirror surface. On the other hand, diffusive reflectance is where the light is effectively reflected at all angles.

The schematic of transmission and reflectance measurement modes in CRAIC 20 system is illustrated in Figure 2-4. The difference in these two modes is the light path in which the UV-visible-NIR light source after coming to sample will transmit (transmission mode) or reflect (reflectance mode) back to the objective to collect the signal. The signal after being collected will go through a grating to separate light with different wavelengths and finally be detected by a cooled CCD detector array. The

signal from CCD will be converted to digital signal by convolution and calibration processes to give final spectra data.

Figure 2-4. Schematic of measurement principle in CRAIC 20 system. (a) Transmission/absorbance mode. (b) Reflectance mode.

CRAIC 20 is an integrated system constructed by building the spectrometer into an optical microscope. However, unlike normal optical microscope which can only operate in the visible range, the optical components of CRAIC 20 are specially made so that they can work in UV-visible-NIR range (200-2000 nm). The micro-spectrometer can magnify and display the sample image as in optical microscope so that we can easily choose the area of interest to be measured. The system also displays the aperture area simultaneously to indicate the location where the spectra will be taken. The sample image and aperture can be seen in Figure 2-5. There are six apertures with different sizes to choose from CRAIC 20. With 36X objective, the smallest aperture is 1.7×1.7 microns and the largest is 33.6×33.6 microns.

Figure 2-5. Aperture image (centered black square) on a single perovskite platelet.

The signal from transmission or reflectance obtained from CRAIC 20 is relative to the reference signal without sample:

$$C = \frac{S - D}{R - D} \quad (2-2)$$

where C is the transmission or reflectance signal, D is the dark scan signal, S is the sample scan signal, and R is the reference scan signal. Because the dark scan is proportional to the scanning time, the dark signal effect would be reduced if shorter scanning time is used. In order to minimize the noise level, the S and R signals should be much larger than D by maximizing incident light intensity. The absorbance can be obtained with the formula:

$$A = -\log\left(\frac{I}{I_0}\right) \quad (2-3)$$

where I_0 is the intensity of radiant energy striking on the sample and I is the intensity of energy emerging from the sample. In fact, I_0 and I are the R and S signals, respectively in the transmission mode.

2.3 Raman/photoluminescence spectroscopy

In this thesis, all Raman and photoluminescence spectra were taken on T64000 Horiba Jobin Yvon micro-Raman spectrometer with a backscattering signal collection configuration. The charge coupled detector (CCD) with the detection range from UV to NIR is cooled by liquid nitrogen. The picture of the Raman system is shown in Figure 2-6 with main components properly labeled. The whole system is placed on a hydraulic noise-reduction optics table to reduce the vibration during measurement. When needed, a cryostat (RC102-CFM Cryo Industries of America) connected with turbo pump and temperature controller can be used to carry out temperature dependence measurement. If liquid helium is used, the temperature can be controlled in the range of 4.5 – 340 K.

Figure 2-6. Horiba JY T64000 micro Raman spectrometer system.

The spectrometer is equipped with 640 mm focal length double subtractive pre-monochromator followed by another 640 mm focal length spectrograph. An Olympus U-5RE-2 confocal microscope is used to view individual micro/nanostructure of interest. The excitation laser beam is aligned through a beam splitter at the microscope which allows the laser to excite the sample below objective and subsequently collects the signal from sample back to the spectrometer. The signal then goes through a pinhole

which is used to adjust the volume of light to be collected based on the laser diameter, sample size, and to eliminate the stray light. The spectrometer can be operated in two different modes: triple grating and single grating depending on the experiment requirement. A simplified optics system of T64000 spectrometer showing principle of the two modes is illustrated in Figure 2-7.

Figure 2-7. The schematic structure of T64000 spectrometer depicting the light path for triple grating and single grating modes.

In the triple grating mode, the polychromatic light (signal after sample excitation) is dispersed by the Grating 1. Then, a motorized slit is used to selectively pass a desirable wavelength range ($\lambda_1 - \lambda_2$). Grating 2 recombines all the dispersed light in the desirable range and focuses it into another slit to produce again a polychromatic light (in the range of $\lambda_1 - \lambda_2$). The Grating 3 disperses the light again before it is detected by

CCD array. The combination of Grating 1 and 2 functions as a tunable, efficient bandpass filter which cuts out all undesirable portion of spectrum (*i.e.*, stray light). Thus, the spectrometer can measure signal as close to the excitation laser line as 4 cm^{-1} . This mode is extremely helpful in the measurement of low frequency Raman and anti-Stoke photoluminescence.

In the single mode, the signal after sample excitation is directly aligned to the Grating 3 after cutting the laser line with a notch filter or a long pass filter (in case of Stoke PL measurement). The advantage of single mode is that the signal collection efficiency is much higher than that of the triple mode. With 1800 gr/mm grating, the spectral resolution of the system can be as high as 0.15 cm^{-1} .

2.4 Excitation lasers

In our lab, we use various types of lasers for sample excitation. With some common wavelengths such as: 471, 532, 671, and 785 nm, solid state lasers are used. For UV excitation, we use He-Cd laser with two possible output wavelengths: 442 nm and 325 nm. An air-cooled Argon laser system is used to produce laser lines of: 458, 488, 502, 514 nm. For more wavelength excitation, two tunable laser is available with the ranges from 700-990 nm (Matisse Ti-sapphire) and 650-780 nm (Matisse Dye laser with Rhodamine 6G). This tunable laser is very helpful in the laser cooling experiment where precise wavelength tunability is desirable. For photoluminescence lifetime measurement and optically pumped lasing experiment, a femto-second laser system (Spectra Physics) is used. The two laser system is shown in Figure 2-8.

Figure 2-8. Laser system in our lab. (Left) Two tunable laser system: Matisse Ti-sapphire and Dye laser. (Right) Spectra Physics femtosecond laser system.

The femtosecond laser system consists of the primary oscillator (MaiTai, Spectra Physics) and amplifier (Spitfire ACE, Spectra Physics) pumped by Nd:YLF laser (Empower, Spectra Physics). The amplifier output is used to seed parametric amplifiers TOPAS and TOPAS White (Light Conversion).

Chapter 3 : Synthesis and characterization of low dimensional perovskite single crystals

At the time I enrolled in my PhD study in 2013, there were several methods reported to prepare organic based lead halide perovskite film which is a suitable form to study optical and electrical properties as well as to fabricate opto-electronic devices.^{1,2,95} The simplest method is spin-casting from a solution of perovskite compounds. However, this method usually gives inhomogeneous, polycrystalline structure with large surface roughness. Thermal evaporation was used to obtain a better homogeneity and higher crystalline perovskite film through either co-evaporation⁹⁶ of lead halide and alkyl amino halide or single source (perovskite) evaporation.⁹⁷ While the former usually incorporates difficulty to balance the two source evaporation rates due to a much higher vapor pressure of organic component compared to the inorganic counterpart, the latter requires dedicated equipment. The third method is to dip pre-deposited lead halide film into a solution of alkyl amino halide to convert lead halide to its corresponding perovskites.⁹⁸ This method works well with layered perovskite compound $(\text{RNH}_3)_2\text{PbI}_4$ in which R- is alkyl with two or more carbon atoms in the chain due to the ease of diffusing alkyl amino halide molecules into the lead halide octahedron network through the van der Waals gap within the organic bilayer and the reaction could be done in minute time. However, in the case of $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskites, due to the lack of van der Waals gap in the three dimensional structure of lead halide, the required dipping time would be much longer (*i.e.*, 1-3 hours). Such a long emerging time in an organic solvent could dissolve and/or disperse parts of lead halide and the formed perovskite, reducing the quality of perovskite film.^{1,99} In conventional semiconductors, there have been extensive investigations of the synthesis in forms of nano-platelets (2-D),¹⁰⁰ nano-wires (1-D),^{101,102} nano-belts (quasi-1D),^{103,104} and their extraordinary optical and

electrical properties compared to bulk counterpart, leading to a number of exciting applications in nano-electronics and nano-photonics. Thus, the need to have high quality, single crystal perovskites, especially the ones at lower dimension for fundamental study is highly demanded. In this chapter, I will present the synthesis of $\text{CH}_3\text{NH}_3\text{PbX}_3$ nanoplatelet and nanowire by two-step CVD method and solution growth of single crystal 2D $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ perovskite.

3.1 CVD synthesis of lead halide nanoplatelets

In order to synthesize perovskite nanocrystal, we start with the growth of its precursor – lead halide using our home-build CVD system. Source material PbI_2 , or PbBr_2 , or PbCl_2 powder (99.999%, Aldrich) was used as a single source and put into a quartz tube mounted on a single zone furnace as described in Chapter 2, section 2.1. The freshly-cleaved muscovite mica substrate ($1 \times 3 \text{ cm}^2$) was pre-cleaned by acetone and isopropanol, and placed in the downstream region inside the quartz tube. The quartz tube was first evacuated to a base pressure of 2 mTorr, followed by a 30 sccm flow of high purity Ar gas premixed with 5% H_2 gas. The temperature and pressure inside the quartz tube were set and stabilized to the desired values for each halide (380 °C & 200 Torr for PbI_2 ; 350°C & 75 Torr for PbBr_2 ; and 500°C & 200 Torr for PbCl_2). In all cases, the synthesis was done within 20 minutes and the furnace was allowed to cool down to ambient temperature naturally.

The reasons we chose muscovite mica as the substrate of the synthesis are as following. First, muscovite mica with the structure 2M_1 poly-type $[\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2]$ ¹⁰⁵ is a layered material. Right before any synthesis, the substrate could be freshly-cleaved to give a perfectly flat and clean surface even without any solvent cleaning. Second, muscovite mica with its hexagonal

symmetry crystalline surface can induce van der Waals epitaxial growth of lead halide crystals in horizontal direction. Finally, muscovite mica has relatively high transparency at the visible range (*i.e.*, > 96% with 200 μm thick film). Thus, we can characterize optical properties of the as-grown crystals on the substrate without the need of a transferring process which usually reduce the quality of the crystals. Other substrates have also been used to synthesize the crystals such as: sapphire, Si/SiO₂, pure Si. However, in all case, the crystals were either too small (*i.e.*, lateral size <5 μm) or too thick. Figure 3-1 shows the optical and SEM images of PbI₂ crystals grown on Si/SiO₂ substrate with optimal parameters in the case of muscovite mica. We can clearly see that the PbI₂ crystal layers stack in vertical direction with uneven surface area. For the sake of optical characterization, we intentionally optimized the parameters to get crystals with flat surface, single grain, and with large enough lateral size (*i.e.*, >5 μm).

Figure 3-1. Optical (Left) and SEM (Right) images of PbI₂ grown on Si/SiO₂ substrate. The scale bar on the left is 50 μm , and the one on the right is 10 μm .

It is noted that the setting temperature we chose to grown the lead halide crystals is slightly lower than the melting temperature at ambient pressure (*e.g.*, setting temperature is 380 °C for PbI₂ (melting temperature: 400°C). This is to ensure the slow evaporation rate of the source which is more favorable for horizontal growth of the crystal. Figure 3-2 shows the optical and SEM images of lead halides grown on

muscovite mica substrates. The difference in color corresponds to different thickness as shown in Figure 3-2b for particular lead iodide platelets. The in-plane orientation of platelets in the case of PbCl_2 and PbBr_2 (Figure 3-2a: A, B) is evident of van der Waals epitaxial growth on muscovite mica substrate due to the three-fold symmetry of mica surface lattices.¹⁰⁶

Figure 3-2. Morphological characterizations of lead halides nano-platelets as-grown on muscovite mica substrate: a) Optical (above) and SEM (below) images of lead halides: A, D: PbCl_2 ; B, E: PbBr_2 ; C, F: PbI_2 . b) Optical images of individual PbI_2 nano-platelets with different colors corresponding to different thicknesses as measured by AFM. c) XRD pattern of the platelets, indexed in blue for lead halides and in red for muscovite mica. d) Raman spectra measured for individual lead halide platelets. *Insets*: Black curves: experimental data, purple curves: simulation data, green curves: peak fitting.

The as-grown lead halide platelets on mica were characterized by powder X-ray analysis (Figure 3-2c) in θ - θ geometry, meaning that only planes parallel to the surface of substrate contribute to the patterns. Multiple strong peaks indexed in red

corresponding to basal planes of muscovite mica¹⁰⁵ while peaks indexed in blue corresponding to PbCl₂, PbBr₂ and PbI₂, respectively. It is noted that, lead halide platelets have highly oriented growth direction along *a*-axis for the cases of PbCl₂ and PbBr₂ and *c*-axis for PbI₂. Raman spectroscopy was used to further characterize the crystalline structure of individual platelet for each lead halide compound. All Raman spectra were taken under 633 nm excitation with laser power of 0.5 mW through 100× objective at room temperature. The Raman spectra of the as-grown lead halide platelets agree well with their corresponding single crystal spectra as reported in the literature.^{107,108} The detail assigned vibrational modes for each spectrum were shown in Table 3-1.

Table 3-1. Assignments for low frequency Raman peaks of lead halide platelets.

Lead halide	Frequency (cm ⁻¹)	Symmetry
PbI ₂	73 96 112	E _g A _{1g}
PbBr ₂	21 34 53 72.8 83.8 99	B _{2g} B _{1g} B _{1g} B _{1g} B _{2g} B _{1g}
PbCl ₂	26 38 59 98.7 132.4 150.6 178.5	B _{1g} A _{1g} + B _{2g} B _{1g} B _{1g} B _{2g} A _{1g} + B _{2g} + (B _{3g}) B _{1g}

The platelets show highly flat and smooth surface with a surface roughness of only ± 1.5 nm as seen by SEM (Figure 3-2) and AFM (Figure 3-3 below).

Figure 3-3. AFM data of PbBr₂(a) and PbI₂(b) showing the surface roughness of grown platelets.

More detailed characterization was also carried out using transmission electron microscopy (TEM) and a scanning TEM (STEM) to assess the structure, crystallinity, and elemental composition of the as-grown PbI₂ sample. Figure 3-4a is a typical TEM image of the PbI₂ platelet; Figure 3-4b and c give the corresponding Pb and I mapping images obtained by energy dispersive X-ray spectroscopy, which confirms the elemental uniformity of the as-grown PbI₂ platelet over the whole platelet. The high-resolution cross-sectional TEM image (see Figure 3-4d) of the platelet shows that the interlayer space is around 0.703 nm, which is in good agreement with the (0001) plane spacing theoretical value.^{109,110}

Figure 3-4. TEM analysis of PbI₂ platelet. (a) Low resolution TEM image of a PbI₂ platelet. (b, c) The element mapping images obtained by energy-dispersive X-ray spectroscopy show the uniformity of the platelet of PbI₂. (d) HRTEM structural analysis of the cross-section of single crystalline PbI₂ platelet, which shows a layer spacing of around 0.703 nm. (e) High resolution TEM (HRTEM) image showing the hexagonal structure of the PbI₂; red dash circle (bright spot) is the top-layer iodine atom, blue dash circle (dim spot) is the lower-layer iodine atom, the center position is the Pb atom. Top inset is a sketch of the PbI₂ structure from the top view; bottom inset is the fast Fourier transform pattern from the HRTEM image.

The atomic structures of the layer atoms in planar view are also studied by high resolution TEM (HRTEM). Figure 3-4e is the HRTEM image of the layer PbI₂, where the middle inset overlapping the structure corresponds to the simulated HRTEM image. Notice that red and blue dashed circles represent the positions of top/lower-layer of iodine atoms, which are indistinguishable from the HRTEM images according to the image simulations performed. In the center position encircled by these iodine atoms is the Pb atom, which is relatively brighter compared to the iodine atoms, which is also in

good agreement with our HRTEM image simulations. Figure 3-4e, bottom inset shows the corresponding fast Fourier transform (FFT) pattern of the HRTEM image showing the six-fold symmetric diffraction spot, which is consistent with our XRD results. All these characterizations attest the high crystallinity of these as-synthesized PbI_2 platelets, which is an important factor for achieving photon amplification in these naturally formed whispering gallery cavities.

Thanks to the naturally layered structure of PbI_2 , it was easier to synthesize its thinner platelets comparing to other lead halide siblings (*i.e.*, PbBr_2 and PbCl_2). By tuning the parameter such as reducing pressure (100 Torr *versus* 200 Torr) and growing time (5 minutes *versus* 15 minutes), it is possible to grown high density, mono and few-layer PbI_2 flakes as illustrated in Figure 3-5.

Figure 3-5. Growth of mono and few-layer PbI_2 flakes. (a) Optical image of high density PbI_2 flake on as-grown mica substrate. Scale bar is 20 μm . (b) AFM scanning of a single PbI_2 flake. (c) Line profile of the AFM scanning in (b) showing the thickness of ~ 0.7 nm, in good agreement with theoretical thickness of PbI_2 .

3.2 Controlled growth of PbBr₂ nanowire array

There have been numerous researches to explore nanowires as new building block in electronics,¹¹¹⁻¹¹³ batteries,^{114,115} photonics,¹¹⁶⁻¹¹⁹ solar cell,¹²⁰⁻¹²² and biological/chemical sensors.¹²³⁻¹²⁵ The advantageous properties of nanowires in these studies are the large surface area, small diameter, smooth surface, and high crystallinity. Controlled growth of nanowires has also enabled biosensors with all detectors and electrodes integrated in a single nanowire during the growth process.^{124,125} One of the advantages of bottom-up synthesis of nanowires is the ability to achieve nanowire heterostructures such as: core/shell heterostructures, and superlattice axial heterostructures. Such structures are extremely difficult to achieve with conventional fabrication methods. Some of the high performance electrical and photonic devices have only been demonstrated in the nanowire form. Thus, the combination of nanowire structure and lead halide perovskite, a material with excellent optical and electrical properties, is worth to be further explored by the research community.

During the preparation of PbBr₂ and PbCl₂ nanoplatelets, we realized that by carefully controlling the parameters, it was possible to obtain high density of nanowire array. The synthesis was done in the same manner with PbI₂ nanoplatelets as described in section 3.1 above. Figure 3-6 shows the SEM images of the products on muscovite mica obtained at different downstream position relative to the center of the tube furnace where the source was placed.

Figure 3-6. CVD growth of PbBr_2 on muscovite mica at different downstream position relative to the tube center.

As we know that, the single zone furnace has uneven temperature profile along the tube. Closer to the center of the furnace, the higher temperature of the tube is. In fact, the thermal couple which detects the temperature is placed in the center of the furnace. As the position is far away the center, especially near two ends of the furnace, the temperature gradually drops. It is noted that, among other parameters (*i.e.*, pressure, gas, flow rate), temperature is the only factor that is different along the tube during the synthesis. As seen in Figure 3-6, the PbBr_2 formed droplet-like particles at around 14 cm, which has been confirmed by Raman that they are actually amorphous rather than crystalline particles. The PbBr_2 only started to crystallize at around 14.3 cm in the form of platelets. As the position went further to the downstream, the PbBr_2 crystals became elongated and finally formed nanowires. Since there was neither catalyst used in our synthesis nor existence of a metal tip at the end of nanowires, the famous nanowire growth mechanism vapor-liquid-solid (VLS) can be ruled out in this case. It is also noted that the nanowires were grown in horizontal direction rather than vertical as in conventional synthesis of nanowires. In addition, most of nanowires were aligned in

exactly the same direction which let us think about the involvement of the substrate in the growth mechanism. Wang *et al.* reported the self-assembly of Pd-based nanowires on muscovite mica substrate.¹²⁶ As we know that muscovite mica surface has a hexagonal structure with a lattice constant of $a_m = 5.18 \text{ \AA}$. In this paper, they attributed the growth of nanowires on muscovite mica to the lattice matching between crystalline structure of mica surface and [010] plane and the epitaxial growth of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ crystal. Matolinova *et al.* also reported the growth of WO_3 nanowires on muscovite mica substrate by thermal evaporation method.¹⁰⁶ The growth was done by heating the WO_3 source at $600 \text{ }^\circ\text{C}$. The mica substrate was placed above the source at a distance between $0.5 - 2 \text{ mm}$. In this case, they proposed a mechanism which involves the formation of K_xWO_3 nuclei. The K^+ ion is from the surface of mica $[\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2]$ in [001] plane. The epitaxial growth of K_xWO_3 is preferably progressed along [001] axis which leads to the formation of nanowire nuclei. Later, the WO_3 will continue to grow layer by layer onto the pre-formed K_xWO_3 nanowires. In these two proposed mechanisms, whether there is chemical interaction between mica and the crystal or just van der Waals force of lattice matching between them, the role of mica substrate is inevitable in the formation of the nanowire array. In our case, we also investigated the lattice mismatch between PbBr_2 crystal and muscovite mica as shown in Figure 3-7.

Figure 3-7. Lattice matching between PbBr₂ and muscovite mica surface.

From all the possible lattice matching as shown in the table in lower left Figure 3-7, we can see that the lowest mismatch in both direction is $a \times 2b$. In fact, the XRD data as shown in Figure 3-2c has confirmed that the c axis is perpendicular to the crystal plane. It is noted that the mismatch along b axis is a lower than that of a axis (*i.e.*, 3.66% comparing to 5.34 %). This difference can be the reason that the PbBr₂ crystals were preferably grown on one direction. In the case of PbI₂, since the crystal has hexagonal structure (*i.e.*, $a = b$), there is no preferable direction and the crystal tends to grow in all three-fold symmetric directions of mica substrate. This explains why in the case of PbI₂, we only obtained triangular and hexagonal shape crystals. The difference in morphology of PbBr₂ crystals at different downstream position as shown in Figure 3-6 above can be explained as following. At 14 cm, the temperature of the substrate is higher than the solidification temperature of PbBr₂ at the specific pressure (50 Torr) and flow rate (30 sccm). As it goes further to the downstream, there are two different factors changed: the decrease of substrate temperature and the lower concentration of the source. As the temperature decreases, the rate of solidification of PbBr₂ will increase. At higher source concentration and lower solidification rate as at the position

14.3 cm, the crystal tends to grow in both direction which results in platelets form. On the other hand, as the source concentration decreases and the rate of solidification increase, the crystal tends to preferably grow in one direction as observed at 14.7 and 15 cm. To investigate further the effect of different pressure, we performed a series of experiment as shown in Figure 3-8. In this case, all other parameters were kept constant.

Figure 3-8. Optical images of PbBr_2 crystal formed on mica substrate at different downstream position and pressure.

At higher pressure, mean free path of gas molecules is shorter, that leads to smaller diffusivity thus evaporation rate is lower. This leads to the decrease in the concentration of the source at higher pressure. This is obvious when we look at the density of the crystals formed on mica at different pressure as shown in Figure 3-8. It is also noted that, at lower pressure, the crystals were grown in higher order (*i.e.*, same direction). Nevertheless, the conditions to obtain nanowire array are mainly temperature of the substrate (*i.e.*, the rate of solidification). We can change the density of the nanowire array (*i.e.*, distance between nanowires) by changing the pressure. The area of highly oriented, uniform nanowire array can be as large as $1 \times 1 \text{ cm}^2$. Figure 3-9 shows the SEM images of PbBr_2 nanowire array at the optimal condition.

Figure 3-9. SEM images of PbBr_2 nanowire array on muscovite mica.

3.3 Conversion of lead halide to perovskite

The conversion of lead halide to perovskite is done by reacting gas-phase methyl ammonium halides with the pre-grown lead halide crystals as described in section 3.1 and 3.2. The methyl ammonium halide source was synthesized by a solution method as following. Reference $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystal grown by solution for comparison was also synthesized.

Synthesis of methyl ammonium halide: Methyl ammonium halides were synthesized in a 50 mL 3-neck round flask equipped with a thermometer, a condenser, and a dropping funnel. First, 11.29g (0.12 mol) of 33 wt % in ethanol solution of methylamine (CH_3NH_2 , Aldrich) was charged into the flask. The solution was then emerged in an ice bath and stirred by a magnetic stirrer. Next, hydrohalic acid solution- HX (23.26 g of 55 wt % HI solution in water (Aldrich); 16.856 g of 48 wt % HBr solution in water (Aldrich); or 9.865 g of 37 wt% HCl solution in water (Aldrich)) was slowly dropped into the vessel through the dropping funnel. The temperature was controlled below 10 °C throughout the reaction by controlling the dropping rate of HX solution and ice

feeding to the ice bath. After completion of dropping, the reaction was further maintained at 20 °C for 2 more hours. The solvents were then evaporated at 78 °C until 1/3 of original volume remained. The precipitates were filtered and recrystallized in diethyl ether/methanol mixture (1:1 v/v) two times. The white crystals were dried at 60 °C for 24 hours and stored in a desiccator.

Solution synthesis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal for Raman comparison: First, $\text{CH}_3\text{NH}_3\text{I}$ (0.01 mol), which was synthesized by the procedure described above, and PbI_2 (0.01 mol) were mixed in 8 mL γ -butyrolactone in a 50-mL round flask. The mixture was stirred at 60 °C overnight to obtain a transparent yellow solution. The solution was then transferred to a glass Petri dish and placed onto a hot-plate at 100 °C. The black crystals were formed as γ -butyrolactone completely evaporated.

The conversion experimental setup is demonstrated in Figure 3-10 below. The converting reaction was done in a quartz tube in vacuum with an inertia carrier gas such as nitrogen or argon. The source was placed in the center of the tube furnace where setting temperature (~120 °C) is normally achieved while the pre-grown lead halide platelets were placed downstream. The pressure was about 20 Torr. Figure 3-10b and c show the crystalline structures of lead halide and perovskite with methyl ammonium (CH_3NH_3^+) as cation. As we can see, both crystalline structures have similar network unit of lead halide octahedrons with lead atom located in the center surrounded by halide atoms. While in lead halide, each octahedron shares two equatorial halide atoms with the neighbors in the same layer and shares one axial halide atom with the neighbors from different layers forming a layer structure, the octahedrons in lead halide perovskite form a 3D network structure in which each octahedron share only one halide atom with the neighbors either in the same layer or different layers. The XRD analysis revealed

the hexagonal structure of lead iodide having a lattice constant $c = 0.695$ nm with orientation perpendicular to the substrate (Figure 3-2, Section 3.1).

Figure 3-10. Conversion of lead halide nano-platelets to perovskites by gas-solid hetero-phase reaction with methyl ammonium halide (CH_3NH_3X , $X = Cl, Br, I$). (a) Schematic of synthesis setup using a home-built vapor transport system. (b) Structure of lead halide in which Pb atoms are at the center of halide octahedrons. (c) Structure of lead halide perovskite $CH_3NH_3PbX_3$ ($X = Cl, Br, I$) (d) Thickness of PbI_2 platelets before (images above data line) and after being converted to $CH_3NH_3PbI_3$ (images below data line).

The perovskite $CH_3NH_3PbI_3$ normally has tetragonal structure at room temperature with a lattice constant $c = 1.244$ nm.¹²⁷ The difference in lattice constant c is due to the insert of methyl ammonium group in the center of eight octahedrons and the relocation of equatorial halide atoms resulting in twisting of lead halide octahedrons as illustrated in Figure 3-10b and c. Interestingly, the thickness of PbI_2 and $CH_3NH_3PbI_3$ platelets (before and after conversion) correlated to each other by a factor of 1.81 (as shown in Figure 3-10d) which agrees well with the two compounds lattice constant ratio along c

axis. Our observation is also in good agreement with previous work on PbI_2 film where the film thickness increases by a factor of 1.75 (from 200 nm to 350 nm) after converting to $\text{CH}_3\text{NH}_3\text{PbI}_3$.¹²⁸ This provides a good way to control the thickness of perovskite platelets by monitoring the thickness of the corresponding lead halide platelets.

In order to confirm whether the conversion of lead iodide platelets into perovskite forms has been done successfully, we investigate the crystalline structure by XRD and the optical properties of the platelets before and after conversion as shown in Figure 3-11. Figure 3-11a shows the XRD pattern of as-grown platelets on muscovite mica substrate before and after conversion) in $\theta-\theta$ geometry. It is clearly shown that after conversion, the identical peaks corresponding to 001, 002, 003, 004 of 2-H lead iodide crystals (space group: $\text{P3m1}(164)$, JCPDS file No. 07-0235)¹⁰⁹ disappeared (marked by the dash-red circle in XRD pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3$) and several new peaks of tetragonal-phase lead iodide perovskite were observed.¹²⁷ Due to strong peaks of mica substrate and slightly twisted structure of lead iodide octahedrons after conversion, we could not observe the peak corresponding to planes perpendicular to c -axis as expected in the XRD pattern. However, the disappearance of PbI_2 peaks confirmed the completed conversion. Raman spectroscopy was conducted before and after conversion (Figure 3-11b). In PbI_2 platelet, the peak at 73 cm^{-1} was assigned for the shearing motion between two iodide layers E_g while the vibration at 97 cm^{-1} was corresponding to the symmetric stretch A_{1g} .¹⁰⁸ On the other hand, Raman spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelet shows a low frequency vibration located at 13 cm^{-1} and a broad band featured at around 215 cm^{-1} . The other vibration peaks of the perovskite are quite similar to that of lead iodide probably due to the similarity in their crystalline structures. Nevertheless, the

perovskite platelets which were converted from PbI_2 platelets showed identical peaks to that of reference perovskite crystal implying that it has the same tetragonal structure with solution grown perovskite crystal.¹²⁷

Figure 3-11. Characterizations of lead iodide platelet after conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. a) XRD pattern of as-grown PbI_2 platelets on muscovite mica (below) and after conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelets (above). b) Raman spectra of the same PbI_2 platelet before (green) and after (red) conversion. The blue curve is Raman spectrum of bulk $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal which was synthesized by a solution method for comparison. c) Optical absorption and photoluminescence (at 77K) of PbI_2 platelet before (black curve) and after conversion to perovskite (red curve) d) PL lifetime of PbI_2 platelet before (blue, rectangular dot) and after (red circle dot) conversion.

Optical absorption and photoluminescence of lead iodide and its perovskite were also characterized in individual platelets having similar thickness (180 nm for PbI_2 and 175 nm for $\text{CH}_3\text{NH}_3\text{PbI}_3$) to minimize the effect of thickness on optical density as shown in Figure 3-11c. It is well-known that lead iodide has an optical absorption at

~500 nm while that of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is 770 nm.^{129,130} Moreover, the absorption coefficient of perovskite is also much higher than that of lead iodide. Our data shows similar observation for the two platelets with identical thickness. In addition, after conversion, the platelet showed strong photoluminescence at room temperature while PL of PbI_2 could be obtained only at low temperature (*i.e.*, < 200K). Figure 3-11c also shows the PL of platelet before and after conversion at 77 K which are consistent with the optical absorption spectrum. One of the properties that make $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite suitable for solar cell application is the long diffusion length of charge carriers which is characterized by time-resolved photoluminescence spectroscopy.^{17,18} The life time of charge carriers in the perovskite is exceptionally long so that they can reach to the electrodes of cells before recombination and therefore reduce the loss. In order to verify this property of perovskite, we carried out the time-resolved photoluminescence of PbI_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelets. The result in Figure 3-11d shows that after conversion, the perovskite platelet has PL life-time more than 400 times higher than that of PbI_2 . In summary, it is confirmed that lead iodide platelet was successfully converted to perovskite by thermally intercalating methyl ammonium iodide. This approach can be applied with other lead halide perovskite with even mixed halide composition as shown below.

Figure 3-12a shows the optical absorption and photoluminescence of different lead halide perovskites synthesized by similar manner with $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelets above. The optical absorption reveals that the band-gaps for $\text{CH}_3\text{NH}_3\text{PbCl}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$, and $\text{CH}_3\text{NH}_3\text{PbI}_3$ are at 3.10 eV (400 nm), 2.34 eV (530 nm), and 1.61 eV (770 nm), respectively, in good agreement with previously reports.^{131,132} All perovskite compounds show strong band-edge photoluminescence at room temperature. Figure 3-12b displays the optical characterizations of the mixed halide perovskites prepared by

intercalating different methyl ammonium halide ($\text{CH}_3\text{NH}_3\text{X}$, with $\text{X} = \text{Cl}, \text{Br}, \text{I}$) into PbI_2 platelets.

Figure 3-12. Optical absorption (dash-line) and room temperature PL (solid line) of converted lead halide perovskite platelets. a) Optical properties of different lead halide perovskites ($\text{CH}_3\text{NH}_3\text{PbX}_3$) showing band-gap of 400 nm with $\text{X} = \text{Cl}$, 530 nm with $\text{X} = \text{Br}$ and 770 nm with $\text{X} = \text{I}$ which are in good agreement with previous reports. b) Mixed halide perovskite platelets prepared by conversion of lead iodide platelets with different methyl ammonium halide ($\text{CH}_3\text{NH}_3\text{X}$).

The results show that $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ have broad absorption covering the entire visible range (400 – 750 nm) while $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Br}_{3-x}$ has only strong absorption in the range of 400 – 550 nm. This may partially explain why tri-iodide and iodide-chloride perovskite are more suitable for solar cell application.^{1,95} The mixed chloride-iodide perovskite also shows a stronger absorption in the regime near UV while pure iodide perovskite has larger absorption near 500-600 nm. This result also suggests that if we use a combination of the perovskites in absorption layer of solar cells, one would obtain a higher photo-to-electric conversion efficiency due to higher absorption in the whole range of visible spectrum. By using our synthesis strategy, it is possible to further tune the composition of lead halide perovskite to obtain optimal material for solar cell application such as co-intercalating mixture of methyl ammonium halides into lead halide.

3.4 Solution synthesis and mechanical exfoliation of 2D perovskites

As discussed in Chapter 1, Section 1.1, 2D perovskite is formed when the structure tolerance factor is larger than ideal value – 1. In other words, it is formed when much larger organic cation is used instead of methylammonium CH_3NH_3^+ . Since the rise of perovskite material, most of attention was directed to 3D perovskite mainly due to its better electric and electronic performances. These properties come from the framework of corner-shared metal halide octahedrons. The 2D perovskite with organic layers sandwiched between the metal halide octahedron layers usually possesses poor electrical conductivity, thus, unable to be applied in electronic devices. Recently, the attention for 2D perovskite has been raised extensively mainly due to its combination with 3D perovskite in solar cell application. It is believed that the long chain organic cation in 2D-3D hybrid perovskite can shield the moisture from environment and thus stabilize the cell while still keeping the electrical performance of 3D framework. In the optical point of view, 2D perovskite is an interesting material with unique multiple quantum well structure. This structure is responsible for the extremely high exciton binding energy in the material (*i.e.*, > 200 meV). Excitons in 2D perovskite are Wannier-type in character and delocalized in the metal-halide framework.¹³³⁻¹³⁵ In addition, like other 2D material, 2D perovskite can also be mechanically exfoliated to mono- or few layers. With the excellent optical properties, 2D perovskite can combine with other 2D materials such as: graphene or TMD to create novel hetero-structure optoelectronic devices. With that being said, one of the goals in this thesis is to synthesize high quality single crystal 2D perovskite and study their optical properties and their potential applications in photonics or optoelectronics.

We chose phenyl ethyl ammonium lead iodide $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ or PhEPbI₄ as a case study. The reason is that this compound is one of the most studied 2D perovskites in literature due to its high stability and excellent optical properties. PhEPbI₄ crystal was grown by a solution method. Stoichiometric moles of two precursors: $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{I}$, and PbI_2 were added in a round flask in gamma-butyrolactone solvent until the solution became saturated. During the addition, the mixture was vigorously stirred by a magnetic bar in a hot oil bath to give clear yellow solution. After that, the round flask was allowed to evaporate slowly at 70 °C in a vented oven for several days. After 3-7 days, the various orange millimeter-sized crystals was collected and dried in vacuum oven at room temperature. The crystals then could be readily used for mechanical exfoliation to a designed thickness for optical measurements and laser cooling experiment. Optical images of as-grown PhEPbI₄ single crystal and after mechanically exfoliation are shown in Figure 3-13.

Figure 3-13. Optical image of (a) as-grown single crystal PhEPbI₄ perovskite and (b) Thin flake of PhEPbI₄ exfoliated from the crystal in (a) on patterned Si/SiO₂ substrate. The scale bar in (a) is 100 μm and in (b) is 10 μm .

Other 2D perovskites and 2D-3D hybrid perovskites used in this thesis were also synthesized in the same manner. The only difference in 2D-3D hybrid perovskite was that $\text{CH}_3\text{NH}_3\text{I}$ was added together with $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{I}$ with specific mole ratio to control the structure of desired 2D-3D perovskite crystals. Figure 3-14 shows the XRD pattern of as-grown PhEPbI_4 which confirmed the layered structure and high crystallinity of the crystal.

Figure 3-14. XRD pattern of solution grown PhEPbI_4 single crystal.

3.5 Summary

In this chapter, I have presented the methods to grow high quality of both 2D and 3D perovskites. By using CVD, high crystalline 3D perovskite crystals in the forms of nanoplatelet and nanowire can be grown with high density. The perovskite nanoplatelet has well-defined shape (*i.e.*, hexagonal, triangular, *etc.*) and thickness varying from few tens of nanometers to few hundreds of nanometers. These nanoplatelets can serve as an excellent platform for optical and electrical properties study. By controlling the parameter, large area, highly oriented nanowire array can also be grown on muscovite

mica substrate. High density, single and few layers PbI_2 flakes can also be obtained through this method. The grown perovskite crystals show excellent photoluminescence properties comparing to their solution processed counterpart.

Millimeter-size single crystal 2D perovskite was also grown by slow-evaporation method which gives excellent crystallinity and purity. Due to the layered structure of the 2D perovskite, the crystal can be easily exfoliated by scotch-tape method to achieve optically-thin perovskite platelet which will be used to study optical properties as well as optically pumped lasing and laser cooling.

Chapter 4 : Optical properties of low dimensional perovskite crystals

In the Chapter 3, I have discussed the CVD synthesis and solution growth of single crystal 3D and 2D perovskites. In this Chapter, I will present the optical studies on these high quality crystals such as: long carrier diffusion length in $\text{CH}_3\text{NHPbI}_3$ nanoplatelet, abnormal bandgap shift and phase transition in 3D perovskite, exciton-binding energy, phonon-assisted upconversion photoluminescence in both 2D and 3D perovskites. These fundamental properties are the foundation for the discovery of perovskite applications in optically pumped laser and laser cooling in this thesis which will be discussed in the next two chapters.

4.1 Diffusion length measurement in single $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet

Our two-step CVD growth method has been shown to produce perovskite samples with good crystallinity as demonstrated by the Raman spectroscopy and XRD characterizations discussed in Chapter 3. In order to prove that our perovskite platelets exhibit higher crystalline quality compared to the conventional solution prepared film, we have measured the electron diffusion length in our platelets using $\text{CH}_3\text{NH}_3\text{PbI}_3$ as a case study. We believe that the charge generation and transportation in perovskite layer are well-correlated with the order and quality of its crystal network. Two groups reported that the diffusion length for solution processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ film is about 100 nm for both electrons and holes.^{17,18} We characterized the electron diffusion length in $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelets using phenyl-C61-butyric acid methyl ester (PCBM) as a

quenching layer. We used similar method that has been reported by Xing, G. *et al.*¹⁸, in which the time-resolved photoluminescence technique was applied.

For time-resolved PL measurements, frequency doubled femtosecond laser pulses (400 nm) from a Coherent Mira Titanium: Sapphire oscillator (120 fs, 76MHz at 800 nm) was used as the excitation source. The time resolved PL spectra were obtained using a streak camera system (Optronis GmbH) configured with a fast synchroscan sweep unit (FSSU1-ST) which has an ultimate temporal resolution of ~2 ps including jitter (or ~6 ps after coupling with a monochromator) at the fastest scan speed of 15 ps mm⁻¹. Typical operating scan speeds in this work was at 100 ps mm⁻¹. The optical transmittance and total reflectance spectra of CH₃NH₃PbI₃ platelet on mica substrate and blank mica substrate were measured using micro-spectrometer (Craic 20/20) with 36× objective and an aperture of 15 μm × 15 μm. The absorption coefficient of CH₃NH₃PbI₃ platelet on mica substrate was calculated using the equation below:¹⁸

$$\alpha = \frac{d_{mica}}{d_{total}} \frac{1}{d} \ln \left(\frac{1-R_{total}}{T_{total}} \right) - \frac{1}{d_{mica}} \ln \left(\frac{1-R_{mica}}{T_{mica}} \right) \quad (4-1)$$

where α , d are the absorption coefficient and thickness of CH₃NH₃PbI₃ platelet, respectively. R_{mica} , T_{mica} and d_{mica} are the substrate reflectance, transmittance and thickness, respectively. R_{total} , T_{total} and d_{total} are the reflectance, transmittance and thickness of mica/CH₃NH₃PbI₃ platelet, respectively.

The electron diffusion length was calculated based on diffusion model which was described by Xing, G. *et al.*¹⁸ using the equation below:

$$N(t) = \frac{2n_0L}{\pi} \exp(-kt) \sum_{m=0}^{\infty} \left(\exp\left(-\frac{\pi^2 D}{L^2} \left(m + \frac{1}{2}\right)^2 t\right) \frac{\exp(-\alpha L) \pi \left(m + \frac{1}{2}\right) + (-1)^m \alpha L}{((\alpha L)^2 + \pi^2 \left(m + \frac{1}{2}\right)^2) \left(m + \frac{1}{2}\right)} \right) \quad (4-2)$$

where $N(t)$ is the total photo-generated charge number within perovskite layer, n_0 is initial charge carrier density, L is perovskite platelet thickness, k is original charge carrier consumption rate without PCBM, D is charge carrier diffusion coefficient, α is absorption coefficient (calculated from equation 4-1).

Figure 4-1. Determination of electron diffusion length in $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelets. (a) Time-integrated PL spectra of as-synthesized $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelet on mica (black curve) and after coated with PCBM layer (red curve). *Inset*: Optical image of the measured platelet ($\sim 20 \mu\text{m}$ edge triangle). (b) Thickness measurement of the platelet using AFM. (c) Time-resolved PL decay transient measured at $760 \pm 10\text{nm}$ for $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelet (green dot) and $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelet/ PCBM (purple dot) after excitation at 400nm . (d) A plot of excitation length versus PL lifetime quenching ratios based on the equation 4-2. Diffusion length is scaled in multiples of $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelet thickness (70 nm).

Figure 4-1 displays the experimental results for the estimation of electron diffusion length in $\text{CH}_3\text{NH}_3\text{PbI}_3$ nano-platelets. Figure 4-1a shows the steady state

photoluminescence spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ platelet with a thickness of 70 ± 5 nm with and without a PCBM layer. The thickness of the perovskite platelet used in the experiment was characterized by AFM as shown in Figure 4-1b. Using a homogenous platelet with a small deviation of $\sim 7\%$, the uncertainties of the diffusion length estimation arising from the large variation of perovskite film thickness^{17,18} could be reduced. Figure 4-1c shows the time-resolved PL decay transient of the perovskite platelet with (purple dots) and without (green dots) a PCBM layer. By fitting the decay dynamics, PL life-time of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (τ_0) and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$ (τ_{PL}) were found to be 6.8 ± 0.4 , and 0.278 ± 0.004 ns, respectively. We then plotted the dependence curve of the charge carrier diffusion length on the PL life-time quenching ratio (Figure 4-1d) obtained from the analytical model above. Using the same conservative approach, the electron diffusion length was estimated to be 210 ± 50 nm, which is longer than the minimally estimated values of at least 100 nm reported earlier.¹⁸ This longer diffusion length can be attributed to high crystal quality of the perovskite platelet prepared by the present method.

4.2 Abnormal bandgap shift and phase transition in $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet

As discussed in Chapter 1, section 1.3.1, lead halide perovskite possesses a unique band structure comparing to conventional semiconductors. This unusual structure of the electronic band in perovskite has been correlated to a number of excellent properties such as: long carrier diffusion length, high carrier mobility, efficient charge transport, and high optical absorption coefficient.⁸⁰⁻⁸² When we studied temperature dependence photoluminescence (PL) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet, we realized that the PL peak was redshifted as decreasing temperature which is opposite to conventional semiconductors

(*e.g.*, GaAs, CdS, TMD). Figure 4-2 shows the temperature dependence photoluminescence and absorption spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$. It has been well studied from literature that $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite goes through two reversible phase transitions as changing the temperature.^{127,136} The first transition happens at ~ 150 K which can be attributed to orthorhombic (lower temperature)-tetragonal (higher temperature) phase transition. The second one occurs around 315 K which is related to the tetragonal-cubic phase transition. However, most of previous studies on phase transition of perovskite used XRD as direct tool to characterize the crystalline structure and thus, phase transition in the perovskite. At the time we characterized the temperature dependence photoluminescence of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet, there was no systematic study in which photoluminescence technique was used to characterize the phase transition of the perovskite. It is expected that different phase of material exhibits different photoluminescence behavior (*i.e.*, peak position, FWHM, *etc.*) due to the difference in the crystalline structure leading to change in the band gap. Our experimental results show that below 100 K, the photoluminescence peak at ~ 750 nm can be assigned to orthorhombic phase. From 100 K to 150 K, the perovskite exhibits a phase transition which leads to the appearance of a lower energy peak at ~ 780 nm (dashed red line), which corresponds to the tetragonal phase. Above 150 K, the higher energy peak vanished and there was only lower energy peak at ~ 780 nm presented. This behavior was consistent with the trend in temperature dependence absorption data (Figure 4-2b) which confirmed that the transition was caused by the material band-gap shift rather than other reasons such as: defect state or failure in measurement. The phase transition can be seen more clearly in Figure 4-2c in which we depicted the PL peak position and intensity evolution as changing the temperature.

Figure 4-2. Temperature dependent photoluminescence (a) and absorption (b) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet. (c) PL peak position and intensity of the perovskite extracted from spectra in (a).

Three zones were clearly illustrated and labeled. By using the photoluminescence technique, we can see that the phase transition was a slow process and it happened in a wide range of temperature rather than sharp change at 150 K as reported in literature. In the phase transition zone (*i.e.*, 100-150 K), both orthorhombic and tetragonal phase can co-exist. This is important if we want to fabricate optoelectronic devices working in wide range of temperature using this material. In fact, thermal stability in perovskite solar cell was a big issue for the community which recently was attributed to tetragonal-cubic phase transition.³¹

Despite the existence of phase transition in the temperature dependence PL (Figure 4-2), it is noted that, in the single phase zone (*i.e.*, below 100 K for orthorhombic, above

150 K for tetragonal), the PL peaks are always blue-shifted as increasing temperature. This behavior may be explained as following.

In general, the temperature dependent band-gap of a semiconductor is a function of two factors: the thermal expansion and the electron-phonon interaction, which can be described by the following equation¹³⁷:

$$\frac{\partial E_g}{\partial T} = \frac{\partial E_g}{\partial V} \frac{\partial V}{\partial T} + \sum_{j,\vec{q}} \left(\frac{\partial E_g}{\partial n_{j,\vec{q}}} \right) \left(n_{j,\vec{q}} + \frac{1}{2} \right) \quad (4-3)$$

where the first term represents the band-gap dependence due to thermal expansion (*i.e.*, lattice expansion or contraction due to variation in the temperature), and the second term represents the contribution from electron-phonon interactions. In the following, we would like to further discuss the dependence of each term in the perovskite using $\text{CH}_3\text{NH}_3\text{PbI}_3$ as an example in detail to understand the abnormal behavior of the band-gap shift.

Figure 4-3. Wave functions of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in its tetragonal phase and the respective energy level (reprinted from reference¹³⁸).

We first look at the wave functions to see how the band-gap in this material is formed as shown in Figure 4-3. Many previous theoretical works^{138,139} have shown that the organic component in the perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) is not responsible for the band-gap but the inorganic part (PbI_6 octahedron). According to a recent study by Zhu *et al.*¹³⁸, the conduction band (CB) (*i.e.*, Γ_6^- energy state) of the perovskite only consists of Pb ($6p$) orbital while I ($5p$) orbital is responsible for the valence band (VB) (*i.e.*, $\Gamma_{6\text{ UPPER}}^+$ energy state). As a result, the interaction between Pb and I atoms or the lattice constant of the PbI_6 octahedron will affect the band-gap of the compound. In most semiconductors, when the temperature decreases, the crystal lattice contracts leading to stronger interaction between atoms and thus, widening the band-gap. This is usually considered as positive thermal expansion. Some semiconductors with negative thermal expansion show opposite band-gap shift.

In $\text{CH}_3\text{NH}_3\text{PbI}_3$, however, the temperature dependent single crystal XRD study¹³⁹ has shown that this material has a positive thermal expansion (Figure 4-4a, b). Moreover, the investigations of the band-edge emission under a high pressure (under which the lattice constant decreases due to lattice contraction) of two other perovskite family members: $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (Figure 4-4c) and $\text{CH}_3\text{NH}_3\text{PbCl}_3$ showed that as the pressure increases (hence, crystal lattice contracts), the band-gap blue-shift¹⁴⁰ (except for relative low pressure where phase transition occurs), suggesting that positive thermal expansion in perovskites would modulate the band gap emission just as in normal semiconductors. However, our temperature dependent PL data show that band-gap shift in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (Figure 4-4d), similar to $\text{CH}_3\text{NH}_3\text{PbI}_3$, is also in opposite trend with normal semiconductors. Therefore, we conclude that the thermal expansion

can be ruled out in the abnormal band-gap shift in these materials, while the electron-phonon interaction is the most probable reasoning.

Figure 4-4. Thermal expansion contribution to the band-gap shift of perovskite. (a), (b) Temperature dependence lattice constant of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (reprinted from reference¹³⁹); (c) PL dependence on pressure of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (reprinted from reference¹⁴⁰); and (d) Temperature dependent PL of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ measured in our group.

Now, we consider and evaluate the second term in equation (4-3). The direct contribution of electron-phonon interactions can be described in a second order perturbation theory, which is often very challenging to calculate directly. As such, many models have been developed to interpret the experimental data, for instance the well-known Varshni empirical model.¹⁴¹ Recently, a two-oscillator model has been developed, which was successfully used to explain the anomalous band-gap shift in

CuCl and PbS^{142,143}. Instead of considering all possible phonon modes in Brillouin zone, this model only counts the most two dominant phonon modes with constant energy (Einstein models). The second term in equation (4-3) now becomes¹³⁷:

$$E_g(T) = E_0 + \frac{S_1}{\Omega_1 M_1} \left(\frac{1}{e^{\Omega_1/k_B T} - 1} + \frac{1}{2} \right) + \frac{S_2}{\Omega_2 M_2} \left(\frac{1}{e^{\Omega_2/k_B T} - 1} + \frac{1}{2} \right) \quad (4-4)$$

where E_0 is the bandgap energy without renormalization; k_B is the Boltzmann constant (8.617×10^{-5} eV.K⁻¹); and Ω , M , S are phonon energy, mass of the oscillator (atomic mass of element) and a constant reflecting the direct contribution of electron-phonon interaction, respectively. Due to large mass difference between lead and iodine atoms, the acoustic mode eigenvectors are dominated by lead displacement, while the optical mode eigenvectors are mainly determined by the iodine displacement. As a result, we can use the atomic numbers of lead and iodine to represent the acoustic and optical phonon modes, respectively. This approach has been successfully used to interpret the bandgap variation and lattice dynamics induced by temperature as well as isotopic replacement in high ionicity semiconductor CuCl (similar to PbCl) and more conventional wurtzite CdS semiconductor^{144,145}. From Raman data¹⁴⁶, we can find two phonon modes: acoustic mode with $\Omega_I = 9$ meV (73 cm^{-1}) represents the vibration of heavier oscillator, the Pb-like phonons ($M_I = 207$); and optical mode with $\Omega_2 = 38$ meV (306.5 cm^{-1}) represents the vibration of lighter oscillator, the I-like phonons ($M_2 = 127$).

If we ignore the effect of thermal expansion and fit the equation (4-4) to our experimental data (*i.e.*, temperature dependent PL) above the phase transition temperature (160 – 340 K), we can find the values of E_0 , S_I , and S_2 , which can serve as quantitative measures to evaluate the contributions of electron-phonon interaction in

terms of the temperature-dependent band-edge emissions. The fitting is shown in Figure 4-5 (left panel) below:

Figure 4-5. Contribution of acoustic and optical phonon-electron interaction on the band-gap shift of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Left panel: Fitting of two oscillator model to our temperature dependence PL data. Right panel: Contribution of each phonon mode on the band-gap shift of the perovskite.

The Figure 4-5 (right panel) displays the plot of the bandgap versus temperature (black diamonds), along with bandgap contribution by two phonon modes using the parameters obtained from the fitting. We noticed that the two phonon mode contributions show opposite trends to the band-gap shift of $\text{CH}_3\text{NH}_3\text{PbI}_3$, *i.e.*, S_1 (acoustic mode) shows blue shift while S_2 (optical mode) shows red shift of bandgap, as temperature is increased. We can conclude from this comparison and our experimental data that the contribution in $\text{CH}_3\text{NH}_3\text{PbI}_3$ due to acoustic mode is larger than that from optical mode, which leads to the overall band-gap blue-shift as the temperature increases. In fact, if we count the contribution of thermal expansion on the band-gap shift into the calculation, the contribution of acoustic mode will be even larger since the thermal expansion contribution causes red-shift of band-gap as temperature increases, as we discussed in the previous section.

In conclusion, we have shown that the abnormal band-gap shift of the perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) is due to the strong electron-acoustic phonon interactions over optical phonon and thermal expansion contribution. This result is similar to the case of CuCl ¹⁴² – a semiconductor with a strong electron-phonon interaction and similar abnormal band-gap shift.

4.3 Exciton binding energy in $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet

Exciton binding energy is an intrinsic physical parameter for semiconductor. If the exciton binding energy is smaller than the thermal energy E_k at a specific temperature ($E_k \sim k_b T$), the exciton is dissociated to individual electron and hole, otherwise the exciton is stable. Therefore, the exciton binding energy is very important for the optical and electronic properties of the semiconductors, particularly for the performance of the room-temperature semiconductor devices. The exciton binding energy of near-infrared semiconductor GaAs, CdTe and InP is 4.2 meV, 10.5 meV and 4.8 meV, which is much smaller than room-temperature thermal energy (~ 26 meV).¹⁴⁷ Therefore, the spontaneous emission efficiency is highly suppressed because of the dominant free electron and hole recombination, which definitely hamper the behavior of room-temperature lasing. It is urgent to explore more near-infrared gain medium with binding energy higher than 26 meV. By using temperature dependence photoluminescence spectroscopy as discussed earlier, we can use the equation below to fit the PL intensity as a function of temperature. From that, exciton binding energy of the material can be deduced.^{148,149}

$$I(T) = R \left[1 - \exp \left\{ -\frac{E_b}{k_b T} \right\} \right] + c \quad (4-5)$$

where, $I(T)$ is the PL intensity at temperature T , E_b is the exciton binding energy of material, k_B is the Boltzmann constant, R and c are constants depending on measurement system. The fitting result is shown in Figure 4-6.

Figure 4-6. The integrated PL intensity as a function of temperature. The experimental data (black solid dots) are well fitted using the equation 4-5.

Temperature-dependent steady-state photoluminescence (PL) spectroscopy is conducted on individual perovskite nanoplatelet on micro-Raman spectrometer (Horiba-JY T64000) in a backscattering configuration with an excitation laser of 633 nm. The full spectra were shown in the previous section 4.2. The temperature is varied from 300 K to 150 K since there is a phase-transition around 150 K as discussed above. As the temperature increases, the PL intensity decreases, which mainly attributed to the thermal dissociation of the exciton in the materials. The red solid lines are fitted using equations (4-5) showing the exciton binding energy of 45 ± 11 meV.

4.4 Phonon assisted upconversion photoluminescence in perovskite

In most of luminescent materials, the emission spectrum usually locates at the longer wavelength site of the excitation wavelength. In other words, the energy of emission photon must be smaller than the excitation photon. This rule is known as Stokes' law, and the difference in energy of these photon is called Stokes' shift. However, in some special case, the emission photon has higher energy than the excited one. This process is called anti-Stokes shift emission and can be categorized in three types: simultaneous two-photon absorption, second-harmonic generation, and upconversion.¹⁵⁰ Among these anti-Stokes processes, upconversion luminescence is perhaps the most important one. This process can be induced by much lower power or incoherent excitation sources such as: continuous wave (CW) lasers, standard halogen lamps, or even focused sunlight.¹⁵¹ Phonon-assisted upconversion involves indirect optical transitions mediated by the annihilation of one or multiple phonons. The upconversion process in semiconductor can be illustrated in Figure 4-7 below.

Figure 4-7. Phonon assisted upconversion process in semiconductor.

In this process, first, the excitation photons with energy $h\nu_p$ create a cold distribution of electron-hole pairs. Next, the electrons and holes redistribute in the excited states by interacting with phonons via thermalization. Finally, the electrons and

holes recombine to give luminescence with photon energy of $h\nu_f > h\nu_p$.¹⁵²⁻¹⁵⁴ This upconversion luminescence is the principle of laser cooling in solid. Thus, the critical condition to realize net laser cooling in a material is that it should have strong phonon-assisted upconversion luminescence. Interestingly, we found out that both 2D and 3D lead halide perovskites possess very strong phonon-assisted upconversion photoluminescence at room temperature. Figure 4-8 shows the upconversion spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and PhEPbI_4 perovskites.

Figure 4-8. Phonon-assisted upconversion spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ excited by 785 nm (a), and PhEPbI_4 excited by 633 nm (b).

It is noted that even with the excitation photon with energy of 386 meV lower than that of fluorescence photon as in case of 2D perovskite (Figure 4-8b), the upconversion luminescence was still very strong. The linear power-intensity dependence of these perovskites as shown in the inset of Figure 4-8a and b indicated that these are single photon process rather than two-photon upconversion luminescence. In other words, these are the phonon-assisted upconversion luminescence in the perovskites. Interestingly, we observe that most of compounds in the lead halide perovskite family possess strong anti-Stokes photoluminescence even with single halide or mixed halide perovskites as shown in Figure 4-9. With the tunability of bandgap for this perovskite

family from ~ 400 to 800 nm by changing the combination of halides, there remains a lot of room for optimization to achieve higher cooling efficiency.

Figure 4-9. Anti-Stokes photoluminescence spectra of different perovskites. (a-c) Excitation wavelength at 785 nm with laser power of 10 μW . (d) Excitation wavelength at 633 nm with laser power of 0.5 mW.

4.5 Summary

In this chapter, important fundamental properties of perovskite have been studied such as: carrier diffusion, abnormal temperature-dependent bandgap shift, exciton binding energy, and phonon-assisted upconversion photoluminescence. Time resolved photoluminescence was used to estimate the carrier diffusion length of perovskite nanoplatelet based on a diffusion model reported previously. The result shows that our nanoplatelet has twice electron diffusion length comparing to that of spin-coated film of the same perovskite due to better crystalline quality. The temperature-dependent bandgap shift and exciton binding energy were studied using photoluminescence spectroscopy. The abnormal bandgap shift of perovskite compared to conventional semiconductor may stem from strong electron-phonon interaction. A giant phonon-assisted upconversion photoluminescence has also been observed which opens up new applications for the material such as laser cooling.

Chapter 5 : Lasing in perovskite nanoplatelets

5.1 Introduction

5.1.1 Introduction to nano/micro-laser

Since the first laser demonstration in 1960 by Theodore H. Maiman,¹⁵⁵ the advances of laser technology has driven unprecedented progress in many scientific research and technological development, such as optical spectroscopy, physical analysis, advance measurement, *etc.* The advances in nanotechnologies and miniature optoelectronic devices have led the research community searching for the way to minimize the laser size. It has been a long journey from the first table gas and crystal lasers to the tiny semiconductor laser that are popular today. The question of how small a laser can be has triggered many exciting researches in the literature.^{116,156-158} The first miniaturized laser concept was the vertical-cavity surface-emitting laser (VCSEL) with the size of several emitting light wavelengths introduced in 1980s. In the next decades, many more concepts were subsequently reported such as: micro-disk laser, photonic crystal laser, and nanowire laser.¹⁵⁶ All of these concepts utilized the difference in the dielectric refractive index to confine light in the cavity, the overall size of laser is larger than the wavelength of the emitting light. The minimum optical mode size is constrained by the diffraction limit.

Figure 5-1. Fundamental challenges involved in the miniaturization of laser.

Using a simple Fabry-Pérot cavity, Figure 5-1 illustrates a generalized laser resonator and the fundamental challenges toward miniaturization of laser. The condition for laser operation is that the electric field amplitude (E_0) at an arbitrary point in the cavity returns to its original value after the light make a round-trip:

$$E_0 \sqrt{R_1 R_2} e^{(G_m - \alpha_i)} e^{i4nL/\lambda_0} = E_0 \quad (5-1)$$

where R_1 and R_2 are the reflectivity of two ends of the mirror; λ_0 resonant wavelength at free space; n is the effective index of the medium; α_i is the propagation loss along central waveguide; L is the length of cavity; and G_m is the modal optical gain. To satisfy the equation 5-1, the imaginary exponent must be multiples of 2π , which lead to the cavity length requirement:

$$L = \frac{\lambda_0}{2n} m \quad (5-2)$$

where m is an integer. Thus the smallest possible cavity length is half of the wavelength (*i.e.*, when $m = 1$). The other component of equation 5-1 gives another requirement for the cavity length L in which the modal gain must compensate the internal loss in the light trip.

$$L = \frac{-\ln(R_1 R_2)}{2(G_m - \alpha_i)} \quad (5-3)$$

The modal gain depends on the active material gain G_a by the relationship:

$$G_m = \Gamma G_a \quad (5-4)$$

where, Γ is the confinement factor which describes the overlap between the laser mode volume (V_0) and the active region volume (V_a) as shown in Figure 5-1. Before lasing, the lifetime of a photon (τ_p) in the cavity is dependent on the parameter of the given cavity as following:

$$\frac{1}{\tau_p} = c \frac{\alpha_i - \left(\frac{1}{2L}\right) \ln(R_1 R_2)}{n} = \frac{2\pi c}{Q\lambda_0} \quad (5-5)$$

where, Q is the quality factor of the cavity, and c is the light speed in vacuum. Thus, at the lasing threshold, the modal gain can be related to the photon lifetime by:

$$\frac{1}{\tau_p} \sim c\Gamma G_a / n \quad (5-6)$$

Even though the small lasers may not be based on propagating modes, many concepts and key parameters can be explained by the simplified model described above.¹⁵⁶ When the size of laser becomes smaller, the internal loss is usually higher due to shorter cavity length. Thus, the active material in these small lasers requires a much higher gain (G_a) comparing to bulk laser. Solid-state materials, especially semiconductors, are the most relevant gain materials for smaller laser because of the high optical gain and electrical injectability. Perovskites with strong optical absorption and emission have been reported to be a good gain material as well.⁴ Given the solution

processability, wavelength tunability, and good electrical performance in the material, perovskites can become a novel class of laser material, especially for nano/micro size lasers.

5.1.2 Whispering gallery mode (WGM) cavity

As discussed above for small lasers, there have been a number of cavity designs proposed to date. The goal of these cavities is to effectively confine the light inside a small space and to minimize the internal loss. The main cavity configurations are depicted in Figure 5-2.

Figure 5-2. Microcavity configurations according to different confinement methods. a) Fabry–Pérot cavity. b) Whispering gallery mode cavity. c) Distributed feedback cavity. d) Photonic crystal defect cavity. Reproduced from Ref¹⁵⁹.

Among the above cavities, WGM has the advantages of a high quality factor, low mode volume, and a large optical density.¹⁶⁰ Because of these properties, the WGM cavity has been widely used to study light-matter interaction at micro/nano scale.¹⁵⁹ Back to the history, WGM concept was proposed more than 100 years ago by Lord Rayleigh.^{161,162} When he studied the acoustic wave propagation in the dome of St Paul’s Cathedral, he found that one could always hear the whisper sound of others at anywhere of the gallery if they stood near to the wall which was attributed to the “stick”

propagation of the acoustic wave along the curved wall. In 1939, Richtmyer first used a microsphere as a WGM cavity to achieve high dielectric resonance.¹⁶³ Only one year after the construction of the first laser in 1960, first WGM micro-spherical laser was reported by Garrett.¹⁶⁴ Since then, many designs of WGM micro-cavities have been proposed such as: micro-disk, optical fibers, hemispheres, micro-capillary, etc.¹⁵⁹

To understand the light confinement in WGM cavity, we can consider a simplified 2D circle model as illustrated in Figure 5-3. In this case, the light propagates near the boundary of the circle by multi-total internal reflection (TIR).

Figure 5-3. A simplified 2D circle model of WGM cavity showing multiple reflection of light. Reproduced from Ref.¹⁵⁹

If we ignore the internal loss of the system, the light travelling around the circle must satisfy the below condition in order to be sustained while others will be eliminated.

$$m\lambda = Ln_{eff} \quad (5-7)$$

where, λ is the wavelength; m is the angular mode number; L is the circumference of the circle; and n_{eff} is the effective refractive index. This equation is the fundamental principle of resonant mode in WGM cavity which is similar to the equation 5-2 discussed above. Since the WGM cavity can support both transverse electric (TE) and

transverse magnetic (TM) modes, the equation 5-7 can be rewritten using the explicit asymptotic formulas for numerical approximation of the resonances.¹⁶⁵

$$\lambda^{-1}(R, n_1, n_r, r, m) = \frac{1}{2\pi R n_1} \left[m + \frac{1}{2} + 2^{-\frac{1}{3}} \alpha(r) \left(m + \frac{1}{2} \right)^{\frac{1}{3}} - \frac{L}{(n_r^2 - 1)^{\frac{1}{2}}} + \frac{3}{10} 2^{\frac{2}{3}} \alpha^2(r) \left(m + \frac{1}{2} \right)^{\frac{1}{3}} - 2^{\frac{2}{3}} \left(n_r^2 - \frac{2}{3} L^2 \right) \frac{\alpha(r) \left(m + \frac{1}{2} \right)^{\frac{2}{3}}}{(n_r^2 - 1)^{\frac{3}{2}}} \right] \quad (5-8)$$

where, n_1 and n_2 are the refractive index of cavity and surrounding environment, respectively; $n_r = n_1 / n_2$; R is cavity radius; r is radial mode number; m is angular mode number; λ is the resonant wavelength; $L = n_r$ for TE modes, and $L = 1/n_r$ for TM modes; and $\alpha(r)$ is the Airy function solution.

To simplify the equation, we assume that the surrounding environment is air which gives $n_2 = 1$. If we only consider the fundamental mode $r = 1$, which is also most frequently observed experimentally, the Airy function solution $\alpha(r)$ will equal to: 2.388.¹⁶⁵ Thus, the approximation for TE and TM mode positions can be derived:

$$\lambda_{TE} \approx \frac{2\pi R n_1}{m + 1.856 m^{\frac{1}{3}} + \left(\frac{1}{2} - \frac{n_1}{\sqrt{n_1^2 - 1}} \right)} \quad (5-9), \text{ and}$$

$$\lambda_{TM} \approx \frac{2\pi R n_1}{m + 1.856 m^{\frac{1}{3}} + \left(\frac{1}{2} - \frac{1}{n_1 \sqrt{n_1^2 - 1}} \right)} \quad (5-10)$$

It should be noted that the angular mode number m is assumed to be large enough so that the terms $\left(m + \frac{1}{2} \right)^{\frac{1}{3}}$ and $\left(m + \frac{1}{2} \right)^{-\frac{2}{3}}$ in equation 5-8 are negligible. The condition for WGM micro-cavity to have internal reflection is that the cavity material should have reflective index larger than surrounding environment (*i.e.*, $n_1 > 1$). Thus,

based on equation 5-9 and 5-10, the TE modes will resonate at longer wavelengths than TM modes for the same angular mode number. The analysis for 3D micro-cavity such as micro-sphere will be more complicated since the light can also resonate in the zigzag paths along the circular cross-section. Nevertheless, in the scope of this thesis where we achieved lasing in 2D nanoplatelets, the above analysis will be still valid.

5.2 Lasing in layered material – PbI₂ nanoplatelets

Lead iodide (PbI₂), which consists of a repeating unit of a hexagonally closed packed layer of lead ions sandwiched between two layers of iodide ions (layered material), has some unique optical and electronic properties that are quite different from traditional semiconductor gain material such as CdS, ZnO, and GaN.¹⁶⁶⁻¹⁶⁹ In these layered semiconductor materials (PbI₂, BiI₃, HgI₂, Bi₂S₃, and Sb₂S₃), spatial confinement of charge carriers in multilayered or multi-quantum-well structures has many potential utilities in photovoltaic, detectors, sensors, and photo catalysis.¹⁶⁹⁻¹⁷¹ Additionally, this kind of layered material would provide us an ideal system to investigate the fundamental properties of excitons in a highly ionic environment and low dimensionality, where the exciton-phonon coupling is expected to be unprecedented compared to conventional semiconductors.^{167,172} On the other hand, PbI₂ has been extensively employed as a stable nuclear radiation detector.¹⁷³⁻¹⁷⁵ It converts the X-ray or γ -ray photons directly to electric charges (current carriers) that are stored in a capacitor in each pixel that improves the quality of the image compared with the traditional phosphorus layer. By working as a scintillation detector, many electron-hole pairs are first generated and thermalized in the conduction and valence bands after the absorption of the X-ray or γ -ray. Then, electrons and holes migrate through the material, trapping at defects may occur, and energy losses are probable because of non-radiative

recombination. Therefore, understanding the behavior of electron and hole under strong light excitation is beneficial to the design of the photodetector under relatively strong X- or γ -ray exposure intensities. Moreover, PbI_2 is one of the precursors to synthesize lead halide perovskites, which have shown tremendous advances in photovoltaics for the past few years and have also been demonstrated as a promising optical gain material for amplified spontaneous emission (ASE) or lasing.^{4,5,176} Deep investigations of the lead halides precursor (*e.g.*, lead iodide) are important toward the understanding of the photophysics of the inorganic-organic perovskites and their applications in emergent devices.^{7,177} From previous literature, the optical and excitonic properties of single crystalline PbI_2 films and thin layers have been previously investigated by steady-state and ultrafast spectroscopy techniques.^{170,178-182} As for their synthesis, several special experimental methods have been developed involving the sol-gel method,¹⁷⁸ vapor deposition method,¹⁸³ and Bridgman's method for growth of PbI_2 single crystals.^{166,184} However, challenges pertaining to the synthesis of regular-shaped single crystalline PbI_2 crystals with subwavelength thickness, ideal for on-chip optical amplifier and lasers integration with planar optoelectronic devices, remain daunting. Despite the limited work on linear optical properties, the studies that focus on the recombination and amplification of photon emission in layered PbI_2 platelets under strong optical excitation are still limited.^{185,186}

In this work, we have synthesized regular-shaped PbI_2 platelet with thickness ranging from 10-500 nm using a chemical vapor deposition (CVD) method as discussed in Chapter 3, section 3.1. The as-prepared single crystalline platelets exhibit a near band edge emission of ~ 500 nm at 77 K. Whispering gallery mode (WGM) lasing from PbI_2 is demonstrated from individual platelets at temperatures from 77-210 K. Lasing modes are supported in PbI_2 platelets as thin as 45 nm, which is the thinnest planar laser ever

reported. Through a comprehensive power-dependent photoluminescence (PL) and time-resolved photoluminescence (TRPL) study, we establish unambiguously that the lasing mechanism originates from biexcitonic recombination.

5.2.1 Lasing in PbI₂ nanoplatelets

An individual PbI₂ platelet was optically pumped using 400 nm wavelength femtosecond laser pulses at 77 K. The optical pump configuration is schematically shown in Figure 5-4a. The pump laser was focused to a spot size of $\sim 40\ \mu\text{m}$ using a $20\times$ objective. Figure 5-4b shows the power-dependent emission spectra of a typical PbI₂ hexagonal platelet (thickness $\sim 150\ \text{nm}$; edge length $\sim 13\ \mu\text{m}$). A broad spontaneous emission band centered at 500 nm with a full width at half-maximum (fwhm) of $\lambda_{fwhm} \approx 6\ \text{nm}$ can be observed under relatively lower pump fluence excitation (*e.g.*, $P < 100\ \mu\text{J}/\text{cm}^2$). With increased pump fluence ($\sim 200\ \mu\text{J}/\text{cm}^2$), a relatively sharp peak centered at around 502 nm with a λ_{fwhm} of $\sim 3.5\ \text{nm}$ appears at the longer wavelength side of the main spontaneous emission peak. When the pump fluence is further increased ($P > 200\ \mu\text{J}/\text{cm}^2$), the emission peak intensity increases sharply, and the fwhm of the emission peak reduces to $\sim 1.4\ \text{nm}$, which exhibits lasing action.^{187,188} The inset of Figure 5-4b shows the peak emission intensity as a function of excitation intensity (light input-light output, or “*L-L* curve”, right axis) and the fwhm of the platelet emission (left axis). At the lasing threshold $P_{th} \sim 200\ \mu\text{J}/\text{cm}^2$, we observed a clear change in gradient in the *L-L* curve with a concurrent sharp decrease in fwhm.

Figure 5-4. Lasing characterizations of whispering gallery mode hexagonal PbI_2 platelet. (a) Schematic representation of a single PbI_2 platelet excited by a focused femtosecond pulse laser. (b) The evolution from spontaneous emission to lasing in a typical PbI_2 hexagonal platelet; the pumping fluence increased from 40 to 400 $\mu\text{J}/\text{cm}^2$. The inset shows power dependence of the integrated intensity and line width of the dominant emission feature, which gives a threshold of $\sim 200 \mu\text{J}/\text{cm}^2$. (c) A streak camera image of PbI_2 platelet emission when the excitation fluence is above the threshold. (d) The decay profiles of the SE and lasing action are fitted using a mono-exponential decay function yielding lifetimes of 68 ± 3 and 9 ± 1 ps for SE and lasing, respectively.

Beyond the threshold, the lasing peak intensity increases linearly with excitation fluence. It should be noted that only one peak is observed in the micrometer cavity, which probably results from the broadening of lasing modes due to the fact that these lasing modes share almost the same threshold at low temperature range. TRPL study is employed (see Figure 5-4c, d) to further validate the occurrence of the lasing action.

Below the threshold, an Auger-limited spontaneous emission lifetime of ~ 70 ps is obtained. Above the threshold, the PL dynamics at the emission peak show a dominant ultrafast decay channel with a lifetime of ~ 10 ps (limited by the system response of the streak camera over the time window) and a small spontaneous emission component with a lifetime of ~ 70 ps.

Figure 5-5. FDTD simulation of the electric distribution inside the cavity for hexagonal PbI₂ platelet. (a) The optical image of a hexagonal platelet with thickness of ~ 150 nm and edge length ~ 13 μm . The scale bar is 5 μm . (b) The optical image in the charge-coupled device (CCD) after filtering of the pump laser line for a pump fluence of ~ 350 $\mu\text{J}/\text{cm}^2$ (above threshold). (c, d) Simulated field distribution at resonant cavity mode of the typical hexagonal PbI₂ platelets using (c) TM and (d) TE mode.

To prove that WGM lasing occurs in the hexagonal shaped PbI₂ platelet, optical mode simulations are performed to study the field distribution in the resonant cavity modes. Optical simulations are performed using commercial finite-difference time-domain (FDTD) simulation software (Lumerical) to study the mode distribution in PbI₂

platelet grown on mica substrate. To simplify the system from 3D to 2D, we introduce the effective index of refraction, mainly the planar waveguide model. Then we simulate the mode distribution in 2D system using the effective index rather than the index of the material. Figure 5-5a shows an optical image of a representative hexagonal PbI_2 platelet with thickness ~ 150 nm and edge length ~ 13 μm , respectively. The PL emission image (the excitation laser was filtered out by a long pass filter) of the same hexagonal PbI_2 platelet above the lasing threshold can be clearly seen in Figure 5-5b. The bright spots at the hexagonal corners indicate the out coupling of the laser pulses at these locations. It suggests that a good mode confinement in the platelet plane is obtained, leading to an in-plane emission. Figure 5-5c and d show the simulation results on the absolute electric field distribution inside the hexagonal platelet (thickness ~ 150 nm; edge length ~ 13 μm) when the transverse magnetic (TM, effective index ~ 2.18) and transverse electric (TE, effective index ~ 1.97) modes dominate, respectively. In these two scenarios, the optical fields are well confined inside the cavities, and reflections between the hexagonal facets/corners result in the formation of the WGMs. However, compared to the TE mode, the TM mode has a larger effective refractive index (the TM and TE modes should not be the same order because the effective index is generally higher for TE than TM mode of the same order) and relatively strong field intensity; thus, a lower lasing threshold can be expected from the TM mode.¹⁸⁹ This is evident from the similarity between the optical image (see Figure 5-5b) and TM mode simulations (see Figure 5-5c). To experimentally prove our simulation result, using confocal microscopy system, we measured the polarization-dependent lasing intensities. The measured polarization-dependent lasing intensity is shown in Figure 5-6.

Figure 5-6. (a) The FDTD simulation of the electric distribution inside the cavity for hexagonal PbI_2 platelet (TM mode). (b) The scattering emission image of the PbI_2 platelet. The 0 and 90 degree axis are defined as shown in b. The white circle is the confocal area where we collected the scattering signal. (c) The measured polarization dependent lasing intensity. The relatively stronger signal along the 0 degree direction suggests that TM mode is dominant, which is consistent with our simulation result.

It can be seen that the lasing intensity shows a maximum when the polarization is along the 0 degree axis, which suggests that the TM mode dominates the signal (if the TE mode dominates, the maximum signal happens when the polarization angle is in 90-degree direction). Another evidence to confirm the WGM mode lasing rather than $F-P$ lasing in the vertical direction is the $1/L^2$ relationship between the platelet edge length (L) and the lasing threshold. The related data and discussion will be shown in detail in the section 5.2.3.

5.2.2 Lasing mechanism and intrinsic properties of PbI_2 nanoplatelet

To elucidate the lasing mechanism, pump fluence dependent time-integrated PL of a single PbI_2 platelet at 77 K is performed, and the results are given in Figure 5-7a. The inset shows a representative PL spectrum (with a pumping fluence $\sim 40 \mu\text{J}/\text{cm}^2$) with two dominant peaks labeled as Peak X and Peak XX, which are deconvolved from the Gaussian fitting of the broad emission peak. The intensity of Peak X (centered at 498 nm) is linearly proportional (slope ~ 0.95) to the excitation fluence when it is below

$\sim 90 \mu\text{J}/\text{cm}^2$ and then increases as the square-root of the excitation fluence above that. On the other hand, Peak XX (centered at 505 nm) exhibits a quadratic dependence with excitation fluence up to $\sim 20 \mu\text{J}/\text{cm}^2$ and then increases almost linearly proportional (with slope ~ 0.9) to the excitation fluence up to $\sim 200 \mu\text{J}/\text{cm}^2$. Beyond that, Peak XX increases super-linearly with pump fluence to yield a lasing action. Such pump fluence dependent emission characteristics of Peaks X and XX closely resemble those of exciton and biexciton luminescence reported for Si, GaN/AlN, and perovskite materials, respectively.¹⁹⁰⁻¹⁹² Therefore, we attribute the emissions at Peaks X and XX to originate from the single exciton and biexciton emission, respectively.¹⁹³ Radiative recombination of a biexciton produces a photon ($\hbar\omega_{XX}$) and an exciton (E_X), and hence, $\hbar\omega_{XX} = E_{XX} - E_X = E_X + \Delta_{XX}$, where E_{XX} is biexciton recombination energy, and Δ_{XX} is the biexciton binding energy.^{194,195} The biexciton binding energy, $\sim 32 \text{ meV}$, can be deduced from the energy difference between the single exciton E_X ($\hbar\omega_X$) and biexciton $\hbar\omega_{XX}$ which agrees with the value of $\sim 30 \text{ meV}$ reported previously.¹⁹⁶ The PL decay transients of the single excitons (Peak X) and the biexcitons (Peak XX) both exhibit a mono-exponential decay behavior (see Figure 5-7b) and can be well-fitted with a single recombination lifetime of $\sim 83 \pm 4 \text{ ps}$ and $47 \pm 3 \text{ ps}$ for the excitons and biexcitons, respectively.^{197,198} The ratio of biexciton lifetime versus that of the exciton is ~ 1.8 ; which is very close to the intuitive relation of $\tau_X / \tau_{XX} = 2$, where a biexciton is treated like a system of two weakly coupled excitons with half the exciton's lifetime.^{199,200}

Figure 5-7. Lasing mechanism and intrinsic properties of PbI₂ platelet. (a) Excitation power dependent emission intensities of Peak X (open triangles) and Peak XX (open squares) in PbI₂ platelet at 77 K. Inset is the Gaussian fitting of PL spectra (at excitation fluence of $\sim 40 \mu\text{J}/\text{cm}^2$) of PbI₂; the black fitting curve is band X, and the red fitting line is band XX. (b) TRPL spectra of Peaks X and XX, and the inset is the corresponding time-energy two-dimensional image of the PL emission. The pump fluence is fixed at $\sim 40 \mu\text{J}/\text{cm}^2$ at 77 K. (c) The lasing spectra of a PbI₂ platelet at different temperatures (77-210 K). (d) Temperature-dependent lasing threshold and lasing wavelength of PbI₂ are summarized. The blue line is the linear fitting, and the red curve is the exponential function fitting result.

After the lasing mechanism was validated to be biexcitonic in origin, we turned our attention to the intrinsic lasing properties (*i.e.*, wavelength and threshold) as a function of temperature. Figure 5-7c shows the normalized emission spectra recorded at the above threshold for a single PbI₂ platelet from 77-210 K, with the pumping fluence of 0.25, 0.4, 0.7, 1.2, and 2.5 mJ/cm², respectively. When the temperature increases to be higher than 210 K, the lasing action ceases for the PbI₂ platelet. As the

lattice temperature varies, the dominant lasing peak redshifts (see Figure 5-7d) from 496 to 510 nm, which suggests a bandgap narrowing.^{141,201} Furthermore, the lasing peak is always located at the longer wavelength side of the broad emission peak. It means that the lasing behavior is always related to the biexciton formation and recombination at this temperature range (77-210 K). The lasing threshold increases from $\sim 200 \mu\text{J}/\text{cm}^2$ to $\sim 2.3 \text{ mJ}/\text{cm}^2$ when the sample temperature increases from 77 to 210 K (see Figure 5-7d). This behavior can be fitted by an exponential function (lasing threshold $\sim e^{(T/T_0)}$) that describes the thermal broadening of the gain spectrum, and we obtain a characteristic temperature of $T_0 = 45 \text{ K}$ for the PbI_2 platelet laser (see Figure 5-7d). This characteristic temperature is the description of the thermal stability of this material, which explains why no lasing can be obtained at room temperature. On the contrary, some conventional semiconductors exhibit higher characteristic temperatures, for example, 90-130 K for ZnO and 160-246 K for GaN.^{202,203}

5.2.3 Thickness-dependent lasing in PbI_2 nanoplatelets

Since the different platelet size (*i.e.*, edge length L) affects the mode confinement and hence the lasing threshold,²⁰⁴ we carefully conducted this study using a series of hexagonal PbI_2 platelets with similar edge lengths (*i.e.*, $20 \pm 2 \mu\text{m}$) while we investigated the thickness-dependent lasing properties. Figure 5-8a-d show the PL spectra from four typical PbI_2 platelets with different thicknesses (40, 120, 200, and 300 nm, respectively) when they are optically pumped by a pulsed laser at 77 K.

Figure 5-8. Thickness-dependent lasing thresholds in hexagonal PbI₂ platelets. (a-d) PbI₂ hexagonal platelets emission spectra with increasing pump fluence from below threshold to above threshold; inset left is the plot of wavelength versus emission intensity, which shows the threshold of the sample; inset right is the optical image of the hexagonal platelet. The scale bar is 10 μm. (e) Thickness-dependent lasing threshold in a hexagonal PbI₂ platelet; two dips or minima located at 122 and 245 nm are observed for low pump thresholds. (f) Decay profile of the biexciton peak (Peak XX) of the PbI₂ hexagonal platelet with different thickness when excited at the same pump fluence of ~60 μJ/cm².

At lower pump fluence, the PL spectra are broad; however, as the pump influence increased above the lasing threshold, a sharp peak at around 500 nm occurs with a fwhm of 1 nm. A plot of the intensity peak versus pump fluence (insets of Figure 5-8a-d) shows the transition from spontaneous to stimulated emission. The corresponding thresholds for the 40, 120, 200, and 300 nm thick PbI₂ platelets are 442, 54, 195, and 280 μJ/cm², respectively. Figure 5-8e summarizes the PbI₂ lasing threshold with different thickness ranging from 45-300 nm. It is very interesting that the lowest lasing

threshold occurs when the layer thickness is ~ 122 nm. In addition, another local minimum is observed at ~ 245 nm.

To investigate the layer thickness dependence of the lasing threshold, the parametric threshold gain, G_{th} , is used here to describe our current system. The expression of G_{th} is defined as follows, $G_{th} = 2\pi n_g / (\Gamma_E \lambda Q)$, where n_g , λ , Γ_E , and Q are group index of the material, resonant wavelength, energy confinement factor, and quality factor, respectively.²⁰⁵ Since this expression originates from the general gain and loss balance conditions for the rate equation, it is valid for all types of cavity modes. In the case of PbI_2 platelets, the group index and resonant wavelength can be treated approximately independent of the platelet thickness. Furthermore, the lasing modes of PbI_2 for different thicknesses have almost the same peak width (~ 1 nm), which indicates comparable Q factors. Therefore, the energy confinement factor Γ_E should play as the dominant role in our scenario. Because of the large edge length (~ 20 μm) of PbI_2 , the WGM loss in the planar direction can be negligible compared to the loss in the vertical direction owing to subwavelength thickness ranging from 40-300 nm. However, in the vertical direction, the top and bottom surfaces of the PbI_2 platelet function as mirrors by forming a F - P cavity itself. This naturally formed F - P cavity holds maximum energy confinement when the cavity length (D) satisfies the following equation, $D \times n_{\text{PbI}_2} = m \times \lambda / 2$ (see the inset of Figure 5-8e), where λ and n_{PbI_2} are resonant wavelength and refractive index, respectively, while m is an integer.^{158,206} Considering that the lasing wavelength is ~ 505 nm and refractive index of PbI_2 at 505 nm is ~ 2.1 , PbI_2 platelets with thicknesses of ~ 120 nm and ~ 240 nm would possess the maximum energy confinement (Γ_E) for thickness in the range from 45-300 nm range, which would then lead to the lowest threshold at these two thicknesses. This is

in good agreement with our experimental observations of the two lowest threshold pump fluences at 122 and 245 nm (see Figure 5-8e). Furthermore, another proof is the biexciton lifetime measurement (with the same excitation power of $\sim 40 \mu\text{J}/\text{cm}^2$) for the PbI_2 platelets of varying thicknesses, as shown in Figure 5-8f. It is interesting to note that the 120 nm thick PbI_2 platelet exhibits the longest biexciton lifetime. Intuitively, this agrees well with the occurrence of the lowest pump threshold as the longer lived biexciton population would facilitate the population inversion and the buildup of lasing in photonic mode lasing conditions. Therefore, we can conclude that the lasing behavior in hexagonal PbI_2 structure is predominately determined by the planar WGM modes and is also partially affected by the thickness of the platelet. Lastly, a plot of hexagonal PbI_2 platelet edge length (L) versus lasing threshold is shown in Figure 5-9.

Figure 5-9. Lasing thresholds versus edge length of the hexagonal PbI_2 platelets. PbI_2 hexagonal platelets lasing thresholds (black triangles) are plotted as a function of edge length. The red curve is the fitting to a $1/L^2$ trend. Inset are the optical images of a group of PbI_2 hexagonal platelets with different edge lengths but comparable thickness of $200 \pm 20 \text{ nm}$; the scale bar inside is $15 \mu\text{m}$.

To minimize the effect of different thicknesses, a series of PbI₂ platelets with comparable thickness (~200 nm) but different edge lengths (from 14-40 μm) were selected for this study (see inset in Figure 5-9). The best-fit line (red curve) is approximately $1/L^2$, which indicates that the lasing threshold is dominantly dependent on the parameter of PbI₂ platelet edge length. Previous studies have shown that both WGM quality factor (Q) and confinement factor (Γ) depend critically on disk diameter.^{205,207,208} Since lasing threshold is inversely proportional to Q and Γ , a $1/L^2$ relationship is expected for platelet edge length and lasing threshold. By considering the thickness-dependent threshold discussion, we know that the lasing threshold scales inversely with the power of platelet edge length, rather than with platelet thickness. This provides clear evidence of WGM lasing rather than F - P lasing in the vertical direction. This conclusion is consistent with our previous simulation results as shown in Figure 5-5c.

5.3 Room temperature NIR lasing in 3D perovskite nanoplatelets

Near-infrared (NIR) solid-state micro/nanolasers are important building blocks for true integration of optoelectronic circuitry.²⁰⁹ Although significant progress has been made in III–V nanowire lasers with achieving NIR lasing at room temperature,^{157,187,210} challenges remain including low quantum efficiencies and high Auger losses. Importantly, the obstacles toward integrating one-dimensional nanowires on the planar ubiquitous Si platform need to be effectively tackled. Here we demonstrate a new family of planar room-temperature NIR nanolasers based on organic–inorganic perovskite CH₃NH₃PbI_{3-a}X_a (X = I, Br, Cl) nanoplatelets. Their large exciton binding energies, long diffusion lengths, and naturally formed high-quality planar whispering gallery mode cavities ensure adequate gain and efficient optical feedback for low-

threshold optically pumped in-plane lasing. We show that these remarkable wavelength tunable whispering-gallery nanolasers can be easily integrated onto conductive platforms (Si, Au, indium tin oxide, and so forth).

5.3.1 Lasing results of $\text{CH}_3\text{NH}_3\text{PbI}_3\text{-aX}_a$ nanoplatelets

Individual perovskite nanoplatelets are optically pumped by a femtosecond-pulsed laser as shown schematically in Figure 5-10a. Clear diffraction patterns of laser source can be seen from the far-field optical images without white-light illumination (blue patterns, Figure 5-10b, bottom panel). The pattern located inside the corresponding nanoplatelets exhibits a smaller area but of a similar shape (Figure 5-10b), indicating good optical confinement from the nanoplatelet WGM cavities. Figure 5-10c shows the power-dependent emission spectra of a typical $\text{CH}_3\text{NH}_3\text{PbI}_3$ triangular nanoplatelet with a thickness of ~ 150 nm and an edge length of ~ 32 μm (optical image, Figure 5-10c, inset).

Figure 5-10. Lasing characterizations of perovskites whispering-gallery-mode nanocavities. (a) Schematic of optical setup. (b) Far-field optical image of two typical $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelets under the illumination of white light (upper panel) and incidence laser (bottom panel). (c) The evolution from spontaneous emission to lasing in a typical $\text{CH}_3\text{NH}_3\text{PbI}_3$ triangular nanoplatelet. Left inset: integrated output emission over the whole spectra range as a function of pumping fluence using log–log scale. Right inset: Photoluminescence decay curve below and above the lasing threshold. (d) Parallel steady-states SE, lasing and time-resolved photoluminescence measurement on $\text{CH}_3\text{NH}_3\text{PbI}_{3-a}\text{Br}_a$ with similar size. Both spectra in the insets (c,d) are normalized using the highest intensity.

Under low pump fluence excitation (for example, $P = 14 \text{ } \mu\text{J}/\text{cm}^2$, gray curve, Figure 5-10c), a broad spontaneous emission band centered at 768 nm with a full width at half-maximum (fwhm) of $\lambda_{fwhm} \sim 54 \text{ nm}$ can be seen. When the pump fluence increases to be $40.6 \text{ } \mu\text{J}/\text{cm}^2$ (dark yellow curve, Figure 5-10c), several sharp peaks centered at $\lambda = 776.7, 779.2, 781.9, 784.3$, and 786.8 nm with a λ_{fwhm} of $\sim 1.2 \text{ nm}$ appear over the spontaneous emission band. The peak line width is comparable with that of reported in room-temperature nanowire and suspended WGM microdisk NIR laser,^{157,187,211} suggesting the occurrence of lasing action. Each peak corresponds to one whispering-gallery cavity mode. The spacing between two adjacent peaks $\delta\lambda$ is almost the same, indicating the same wave-guiding origin of the modes. As the pump fluence is further increased ($P = 42$ and $51 \text{ } \mu\text{J}/\text{cm}^2$), the lasing intensity increases correspondingly and the lasing mode exhibits a slight blueshift. The detailed waveguide type and lasing mechanism will be discussed later. The *log–log* scale plot of emission output (P_{out}) versus pumping fluence shows a “S”-like curve, which can be well fitted with two linear functions in the spontaneous emission and lasing regimes (Figure 5-10c, left inset). Furthermore, a lasing threshold of $P_{th} \sim 37 \text{ } \mu\text{J}/\text{cm}^2$ is deduced, which is in good agreement with the appearance of the narrow peaks around the pumping

fluence. Time-resolved PL study is also conducted (Figure 5-10c right inset). Below the threshold, the PL decay curve shows a long average lifetime of ~ 2.6 ns, indicative of the characteristics of the spontaneous emission, while an ultrafast decay channel with a lifetime of ~ 80 ps (limited by the system response of the streak camera over the time window) dominates above the threshold pumping due to the occurrence of exciton population inversion and lasing action.

Room temperature near-infrared lasing is also achieved for $\text{CH}_3\text{NH}_3\text{PbI}_{3-a}\text{Br}_a$ as shown in Figure 5-10d with a threshold of $\sim 128 \mu\text{J}/\text{cm}^2$. Several lasing peaks are observed around 785 nm with mode spacing consistent with each other, also suggesting the dominance of WGMs in the perovskites. Although the threshold of $\text{CH}_3\text{NH}_3\text{PbI}_{3-a}\text{Br}_a$ is higher than that of the $\text{CH}_3\text{NH}_3\text{PbI}_3$, for the similar crystal size the fwhm of its lasing mode is smaller (~ 0.9 nm), thus the cavity quality factor ($Q \sim 900$) is somewhat larger (Figure 5-10d). Moreover, our measurement in many $\text{CH}_3\text{NH}_3\text{PbI}_{3-a}\text{Br}_a$ nanoplatelets suggests that lasing with fewer modes is readily achieved, suggesting the potential of single-mode lasing, although the mechanism deserves further in-depth investigations.

5.3.2 WGM analysis of perovskite nanoplatelets

Optical mode simulations are performed to further understand the lasing in the perovskites. Figure 5-11a shows the photoluminescence image of an individual hexagonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet above the lasing threshold. The lasing only couples out at the cavity edge, suggesting a good mode confinement in the plane of the nanoplatelets, yielding an in-plane emission. Figure 5-11b and c show the absolute electric field distribution inside the hexagonal nanoplatelet (thickness ~ 150 nm; edge length $\sim 10 \mu\text{m}$) when the transverse magnetic (TM) and transverse electric (TE) modes

dominates, respectively. In the two cases, the optical fields are well-confined inside the cavities and reflected between the polygonal facets to construct WGM waveguides. With decreasing nanoplatelet thickness, the effective index of the two photonic modes decreases, yielding a higher radiative loss or even the cutoff of the photonic modes, while TM mode has a large effective index thus a lower lasing threshold is anticipated. Experimentally, the lasing cutoff thickness at room temperature is ~ 70 nm, while this value can be pushed to ~ 40 nm at lower temperature (~ 77 K) because of the higher optical gain.

Figure 5-11. Whispering-gallery mode analysis of the perovskite nanoplatelet laser. (a–c) Far-field lasing image (a), simulated field distributions at resonant cavity mode (b: transverse magnetic mode; c: transverse electric mode) of typical hexagonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelets. (d) Lasing spectra of hexagonal $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelets (upper panel) and the lasing mode evaluation as pumping fluence (bottom panel). (e) Lasing spectra is dependent on the edge length of a triangular $\text{CH}_3\text{NH}_3\text{PbI}_3$ whispering-gallery cavity. (f) The wavelength of lasing modes (pink star dots) and Q-factor (dark yellow dots) as a function of the triangular cavity edge length.

The cavity resonant mode λ and the corresponding mode number N are deduced by the equation:²¹²

$$N_{\lambda} = \frac{\left[3(3n_{\lambda}D)^{\frac{1}{2}} \right]}{2\lambda} - \frac{\pi}{6} \tan^{-1} [n_{\lambda} (3n_{\lambda}^2 - 4)^{\frac{1}{2}}] \quad (5-11)$$

where D is the diameter of the circle that circumscribes the polygon cavities, and n_{λ} is refractive index at the resonant wavelength. The experimental values agree well with the theoretical ones, confirming the occurrence of WGM lasing (Figure 5-11d, upper panel). When the pumping fluence is close to the lasing threshold ($40.6 \mu\text{J}/\text{cm}^2$), only TM mode achieves lasing because of the lower gain threshold. As the pumping fluence increases from 40.6 to $50.4 \mu\text{J}/\text{cm}^2$, the lasing of more resonant modes is realized because of the achievement of threshold gain at a high carrier-density. Additional lasing peaks appear near the TM modes (indicated by arrows, Figure 5-11d, bottom panel), which is identified as TE mode. Besides, the lasing modes (that is, 793.1 nm) are slightly blue-shifted (that is, 792.6 nm), which may be due to a band-filling mode or refractive index variation (Figure 5-11d, bottom panel).^{198,213}

For the nanoplatelets of different sizes, the lasing modes can be tuned due to the intrinsic self-absorption of the excitons. As the edge length L increases from $28, 32, 38$ to $47 \mu\text{m}$ (thickness of $\sim 150 \text{ nm} \pm 10 \text{ nm}$), the highest optical gain area where lasing can be realized moves to the lower energy region (Figure 5-11e). The strongest lasing modes of the nanoplatelets are extracted and show an exponential decrease function of the edge length according to the self-absorption equations (Figure 5-11f).¹⁸⁸ The limit of the lasing modes occurs at $\sim 790 \text{ nm}$ as deduced from the fitting, which is close to the Urbach tail near the bottom of the absorption edge, thus further validating the self-absorption dependent lasing mode. Besides, the Q -factor (calculated by λ / λ_{fwhm})

increases linearly from 650 to 1320 with the increase of platelet edge length. For an m -faceted polygonal WGM cavity, the Q -factor of a resonant mode λ is proportional to L/λ .²⁰⁷ Here λ can be considered as a constant; therefore the Q -factor has a linear relationship with the edge length (Figure 5-11f). Although the perovskite nanoplatelet has a subwavelength thickness (40–150 nm), the Q -factor of the on-substrate laser is relatively higher than that reported in suspended microdisk WGM, nanowire,^{157,211} and the recent polycrystalline perovskite thin film DBR NIR lasers,⁵³ suggesting that the large cavity scattering and radiation loss is well overcompensated by the high optical gain of the materials.

5.3.3 Integration of perovskite laser onto different substrates

To prove the potential of integration onto optoelectronic chips, we demonstrate the functional lasing onto other conductive bases such as Si, Au, and indium tin oxide (ITO). Because our perovskites are grown on a transparent insulating substrate, the integration can be accomplished via a simple reversing of the substrate onto the bases without any releasing process or change of pumping method (Figure 5-12a,b) with the same $\text{CH}_3\text{NH}_3\text{PbI}_3$ hexagonal nanoplatelet (thickness ~ 110 nm; edge length ~ 33 μm).

Figure 5-12. Integration of perovskite nanoplatelet laser onto different substrates. (a) Schematic of the integration process of the perovskite nanolaser device onto the

substrates. The transparent mica substrate is reversed and covered onto the Si, Au, and ITO bases. (b) The integrated mica-perovskite laser devices on Si, Au, and ITO substrates. (c-d) Lasing spectra (c) and SE decay curves (d) for the nanolaser devices on different substrates.

Room-temperature lasing is realized on all four substrates (Figure 5-12c). Because the thickness of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is smaller than its diffusion length (~ 200 nm), the spontaneous emission lifetimes decrease gradually from mica (2.89 ns), Si (2.6 ns), ITO (1.9 ns), and Au (1.2 ns) because the electrons are likely quenched on the conductive bases (Figure 5-12d). However, the lasing behavior is not that sensitive to the bases. The threshold of the four types of nanoplatelet laser is almost the same as $\sim 40 \mu\text{J}/\text{cm}^2$, and the lasing peaks (position and relative intensity) exhibit little difference. This is because the exciton avalanche occurs in a much shorter time-scale (< 80 ps) than that of the carrier transfer/trapping at the surface/interfaces. The stable and well controlled lasing behavior of these planar perovskites on the different bases shows great promise for the related on-chip integration.

5.4 Lasing in layered perovskites

As discussed in Chapter 1, section 1.1, metal halide perovskite has two types of structure motifs: 3D and 2D (or layered). Since the “perovskite fever” in solar cells, most of research efforts have been focused on the 3D perovskites.^{1-3,13,95} The reason is that the electrical properties of the perovskite such as: charge transport, carrier mobility, etc. are coming from the lead halide octahedron framework. In 2D perovskite, these lead halide octahedron layers are separated by long chain organic ammonium groups, thus limiting the electrical properties. Indeed, the difference in physical properties of 2D and 3D perovskites can be summarized in Table 5.1 below:

Table 5.1 Comparison between physical properties of 2D and 3D perovskites

Properties	2D	3D
Absorption	Excellent	Excellent
Photoluminescence	Excellent	Excellent
Coupling strength	Up to 200 – 400 meV	~ 30-70 meV
Diffusion length	Short (due to MQW structure)	100 nm ~ 1 μ m
Conductivity	Poor	Good
Mobility	Poor	Good
Film preparation	Easy to infiltrate organic component due to layer structure	Difficult, 3D network block the infiltration of organic
Stability	Good	Poor
Bandgap tunability	Yes	Yes

Figure 5-13. Absorbance and photoluminescence of PhEPbI₄ perovskite at room temperature. The PL was measured with the 458 nm laser excitation.

The large exciton binding energy of 2D perovskite (*i.e.*, 200 – 400 meV) is attributed to the multiple quantum well (MQW) structure caused by the different in

electronic gaps between the metal halide octahedron layers and the organic layers. The exciton binding energy is much larger than the room temperature thermal energy of 26 meV, leading to the localization of the electron-hole pairs in this material. This can be clearly seen in the absorption spectrum of 2D perovskite at room temperature as shown in Figure 5.13. The exciton peak is exceptionally sharp due to the high density of localized electron-hole pairs. Similar to its cousin (*i.e.*, 3D perovskite), 2D perovskite also possesses excellent optical properties such as strong absorption coefficient and photoluminescence (Figure 5.13). It suggests that 2D perovskite can also be a good gain material for possible applications in light emitting diodes and lasing. However, up to date, there are almost no report on lasing of 2D perovskite except only one early report by Kondo *et al.* in 1998.¹⁹² In that work, the authors claimed to achieve lasing of PhEPbI₄ at 16 K using a Ti/SiO₂ planar waveguide. However, the lack of high quality data and thorough explanation in the work make the results unreliable. In fact, the “lasing” spectrum in the report could be just a case of luminescent microcavity or wave-guiding effect.²¹⁴ Nevertheless, this is the only paper that reported an optical gain in the 2D perovskite up to date. Recently, Chong *et al.* revisited the issue and the result was published in PCCP.²¹⁴ In this work, modern and more sophisticated instruments have been used in order to achieve lasing in 2D perovskite than the work by Kondo *et al.* For instance, higher power, femto-second pulse laser was used as excitation source comparing to nano-second pulse laser used by Kondo *et al.* Nevertheless, no lasing was achieved in 2D perovskite even at as low temperature as 10 K. The authors attributed this to low damage threshold of the material and estimated the amplified spontaneous emission (ASE) threshold to be 1.4 mJ/cm², around 10 times that of the damage threshold.

In this work, I will present the lasing achieved in exfoliated PhEPbI₄ flakes at 80 K with relatively low lasing threshold of $\sim 100 \mu\text{J}/\text{cm}^2$. The longer carrier lifetime and lack of trapping states in our single crystal 2D perovskite comparing to previously reported value may be favorable for inversion population process which are attributed to the high crystalline quality in our sample. Moreover, we also present the lasing in several 2D-3D hybrid perovskites at various temperatures up to 200 K. Our work will contribute to the understanding of 2D perovskites as a gain material which is applicable in light emitting devices.

5.4.1 Lasing results in 2D perovskites

Unlike previous attempts to achieve lasing in 2D perovskites where a spin-coated polycrystalline film was used,^{192,214} we used a single crystal of PhEPbI₄ 2D perovskite grown by solution method as described in Chapter 3, Section 3.4. The bulk crystal was then subjected to mechanical exfoliation to get desired shape and thickness flakes on a Si/SiO₂ substrate. The lasing experiment on the 2D perovskite flake is shown schematically in Figure 5-14a. In this case, we used 460 nm femto-second laser excitation with the frequency of 1 KHz to excite the sample. The reason we used 460 nm instead of 400 nm excitation is to minimize the heating effect on sample. We intentionally chose the flakes with regular shapes (*i.e.*, square, rectangular) in order to maximize WGM reflection inside the sample as shown in Figure 5-14b. No external cavity or waveguide layer was used in our experiment. Figure 5-14c shows the PL spectra at different pumping fluences at 30 K. Below lasing threshold (*i.e.*, $< 100 \mu\text{J}/\text{cm}^2$), there are only two broad peaks at 528 and 537 nm with the full width half maximum (fwhm) of ~ 2 and 4 nm, respectively. The origin of these two peaks will be discussed in detail later. When the pumping threshold is larger than $100 \mu\text{J}/\text{cm}^2$, multiple peaks with narrow gaps (Figure 5-14c and its left-inset) appear on the longer

wavelength of the 537-peak. The fwhm of the strongest lasing peak is shown in Figure 5-14d to be only 0.26 nm corresponding to a Q -factor of 2080. The integrated PL intensity dependence on pumping fluence is plotted in the right-inset of Figure 5-14c which shows the “S-shape” curve – an indication of lasing action.

Figure 5-14. Lasing in PhEPbI₄ 2D perovskite flake at 30 K. (a) Schematic of lasing experiment. (b) Optical image of the 2D perovskite flake. Inset: PL image of the flake above lasing threshold. (c) Lasing spectra evolution at different pumping fluence at 30 K. Left inset: Zoom-in spectra from 538 – 541 nm. Right inset: Integrate PL intensity versus pumping fluence. (d) fwhm of the strongest lasing peak in (c).

5.4.2 Exciton origin and trap-state in single crystal 2D perovskite

As mentioned earlier, when the 2D perovskite was excited with femto-second laser (high power density), we observed two peaks at 528 and 537 nm. This is different with the PL spectrum when the material was excited with cw laser at the same wavelength

(*i.e.*, 460nm) in which only peak at 528 nm was observed. To understand the origin of these peak, we carried out the power dependence below lasing threshold using the same femto-second laser excitation. The result is shown in Figure 5-15.

Figure 5-15. Power dependence PL of 2D perovskite excited with fs-laser at 30K. Peak 1 (P_1): 528 nm, and Peak 2 (P_2): 537 nm.

The integrated PL intensity dependence on pumping fluence was extracted from PL spectra and plot in the inset of Figure 5-15. As we can see, peak 1 (P_1) located at 528 nm has a linear intensity dependence on pumping fluence while peak 2 (P_2) located at 537 nm has a quadratic intensity dependence below pumping fluence of 100 $\mu\text{J}/\text{cm}^2$. Above this fluence, P_2 intensity follows a linear dependence on pumping fluence. This characteristic of P_1 and P_2 is similar to the case of PbI_2 which has been discussed in detail in Section 5.2. Thus, we attributed the origin of P_1 and P_2 to be exciton and biexciton of the 2D perovskite, respectively. This result also agrees well with previous reports on the biexciton peak of the 2D perovskite.^{192,214} It is noted that in our case,

there is lack of a surface bound exciton peak located at 535 nm as reported for solution-processed 2D perovskite film.²¹⁴ This can be attributed to the high crystallinity and fresh surface of our exfoliated 2D flake.

To confirm the high quality of our sample, we prepared a spin-coated 2D perovskite film as reference to perform comparative PL and TRPL study. Figure 5-16 shows the PL spectra of 2D perovskite prepared by different method at 78 K.

Figure 5-16. PL spectra of PhEPbI₄ perovskite at 78 K: (a) solution spin-coated film, and (b) Exfoliated single crystal flake.

As we can see that, for spin-coated film, there are two additional peaks at the longer wavelength located at ~ 555 and 690 nm. These peaks can be assigned to the trap-state of 2D perovskite which has been extensively studied by Wu *et al.*²¹⁵ Meanwhile, in our exfoliated single crystal flake, there is no defect peak observed in the longer wavelength regime. It is also noted that the relative intensity of the single crystal sample is ~10 times higher than that of the film (As shown in Figure 5-16, the PL spectrum of single crystal sample is peaked at 10 K with only 1 μW excitation while that of the film is 7 K at 8 μW excitation. The measurements were done in the same setup, thus the collection efficiency was identical). It means that the gain in the single crystal flake is

much higher than that of the film which is favorable for lasing action. We also performed TRPL study on these two samples. The result is shown in Figure 5-17.

Figure 5-17. Comparison between life-time of single crystal (blue) and spin-coated film (pink) 2D perovskite.

It can be clearly seen that the lifetime of the single crystal sample is much longer than that of the thin film. The TRPL curves can be fitted with single exponential function giving the lifetimes of $\sim 4.6 \pm 0.2$ ns and $\sim 202 \pm 40$ ps for single crystal and the film, respectively. The lifetime of the 2D perovskite film reported in the literature is also around 10-100 ps.^{214,215} The exceptionally long lifetime in our 2D perovskite sample is favorable for the inverse population process in lasing action. The longer lifetime also confirms the high crystalline quality and lack of defect in our sample which are responsible for the observation of lasing.

5.4.3 Lasing in 2D-3D hybrid perovskites

We also grew 2D-3D hybrid perovskite single crystals and achieved lasing in these crystals. The general formula for the hybrid perovskite is $(\text{PhE})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, where n is the number of PbI_6 octahedron layer connected to each other in the 2D perovskite.

The structure of the 2D-3D perovskite with different n is shown in Figure 5-18a. We realized that with $n > 3$, it was extremely difficult to control the single structure in the resulted crystals. With $n = 1-3$, the crystals exhibit single PL peaks as shown in Figure 5-18b. However, with $n > 3$ (*i.e.*, $n=4, 5, 6$), the PL peaks are much broader and all located around 750 nm. The peak analysis for $n = 4$ is shown in Figure 5-18c in which multiple peaks can be fitted to the PL spectrum. These peaks can be assigned to different 2D-3D structures (*i.e.*, different n) in the grown crystal. Thus, in the scope of the thesis, we will only consider the single structure crystals up to $n=3$.

Figure 5-18. Structure and PL spectra of 2D-3D perovskites $(\text{PhE})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$.

The 2D-3D hybrid perovskites also have layered structure, thus can be easily exfoliated using the Scotch-tape method. The lasing experiments of the 2D-3D perovskite flakes were done in the same manner as for 2D perovskite described above. The lasing spectra of the perovskites corresponding to $n = 1, 2, 3$ at 80 K are shown in

Figure 5.19. It is noted that the lasing thresholds of perovskites with $n = 2, 3$ are much smaller than that of the pure 2D perovskite $n = 1$ ($\sim 1\text{-}4 \mu\text{J}/\text{cm}^2$ as compared to $\sim 100 \mu\text{J}/\text{cm}^2$).

Figure 5-19. Lasing spectra of 2D-3D hybrid perovskites with $n = 1$ (a); $n = 2$ (b); and $n = 3$ (c).

The lasing can be achieved at much higher temperature for $n = 2$ and 3 (*i.e.*, up to 200 K) while for $n = 1$, the maximum lasing achievable temperature is 80 K, probably because the lasing threshold is approaching to damage threshold of the material. The temperature dependence lasing was carried out for $n = 2$, and the results are shown in Figure 5-20.

Figure 5-20. Temperature dependence lasing in 2D-3D hybrid perovskite with $n = 2$.

The lasing spectra at different temperatures are shown in Figure 5-20a. It is clearly shown that, as the temperature decreases, the lasing threshold also decreases. This is understandable because normally the material gain is higher at lower temperature. It is also noted that while the higher energy peak (*i.e.*, ~ 580 nm) is redshifted as the temperature decreases, the lower energy peak (*i.e.*, ~ 590 nm) where the lasing action happens is blueshifted. This may be due to the peak broadening of the biexciton peak at higher temperature and higher excitation fluence which is similar to the case of PbI₂ and 2D perovskite as discussed above. However, this conclusion needs to be provided with more evidences. In the Figure 5-20b, we plot the dependence of lasing threshold on the temperature. From that, we can calculate the characteristic temperature (T_0) of the 2D-3D perovskite by fitting the equation $P_{th} \sim e^{T/T_0}$ giving $T_0 = 45$ K. Interestingly, the result is very similar to the case of PbI₂ as discussed in Section 5.2 which explains why we can only achieve lasing at maximum temperature of 200 K.

5.5 Summary

We have demonstrated WGM lasing in single crystalline hexagonal PbI₂ platelet fabricated using CVD method. Through power-dependent PL and TRPL studies, we establish that the lasing mechanism originates from biexciton recombination. Platelet thickness dependent lasing measurements reveal that the lowest threshold of lasing occurs when the thickness of the platelet is ~ 120 nm for a series of PbI₂ platelets with comparable edge length. This thickness dependent behavior of threshold can be well explained by the reflection enhancement in the F - P resonance cavity in the vertical direction as validated by the lifetime measurements. Our results demonstrate the feasibility of planar coherent light sources based on layered semiconductor materials,

and the thickness-dependent threshold study is of vital importance for the optimization of layered material based optoelectronic devices.

We have realized room-temperature near infrared solid-state nanoplatelet lasers using the organic– inorganic lead halide perovskites nanoplatelets. The large exciton binding energy, long diffusion length, as well as promising quantum yields of the family leads to strong, stable, and well-controlled lasing actions. The whispering-gallery type planar perovskite nanoplatelet lasers have pronounced optical gain and tunable optical modes, which can be potentially integrated with the existing Si technologies. Our research opens alternative routes beyond III–V nanostructures in achieving near-infrared solid state nanolasing and will inspire more designs of low-threshold near-infrared nanolasers pumped optically and electrically.

We have also shown that it is possible to achieve lasing from the biexciton peak in the exfoliated 2D perovskite without using any external cavity or waveguide layer. The result is attributed to the high crystalline quality and the lack of trap state in the single perovskite crystal. The super long PL lifetime in our 2D crystal may be responsible for the carrier inversion population in lasing action. We also demonstrate that lasing is achievable for 2D-3D hybrid perovskite at maximum temperature of 200 K. This can provide the way to tune the lasing wavelength in the green-red regime. Our results are significant for the research of 2D perovskite as a light emitting material and open up the possibility to utilize this material in opto-electronic applications.

Chapter 6: Laser cooling in perovskite single crystals

6.1 Introduction to laser cooling

Optical irradiation with suitable energy can cool solids, a phenomenon known as optical refrigeration proposed in 1929²¹⁶ and experimentally achieved in ytterbium-doped glasses in 1995.²¹⁷ Since then, high-power cooling experiments and the development of integrated solid-state optical cryocooler devices have continued to utilize exclusively Yb³⁺-doped YLiF₄ (YLF:Yb) crystals. YLF is attractive because it can be doped with a high concentration of Yb³⁺ (replacing Y³⁺ at typically 5–10 mol%), has a sufficiently low phonon energy to ensure a high quantum yield of the ²F_{5/2} excited state of Yb³⁺, can be prepared in high purity and optical quality, and is chemically, mechanically, and thermally rugged. The record-low temperature for cooling YLF:Yb has steadily fallen from 119 K in 2013²¹⁸ to the sub-100 K regime in 2014 (93 K)²¹⁹ and 2015 (91 K),²²⁰ the latest result being the current world record (Figure 6-1a). These experiments have typically used a pump laser delivering ~50 W at 1020 nm to excite the ²F_{7/2}(E4)→²F_{5/2}(E5) crystal-field transition of Yb³⁺ in $\vec{c} \parallel \vec{E}$ polarization with the YLF:Yb crystal placed inside a non-resonant cavity as shown in Figure 6-1b.

In parallel, numerous research groups have continued to explore new and to study existing laser-cooling materials, both theoretically and experimentally. Fluoride crystals and glasses remain a focus of current research. Zhong *et al* have reported laser cooling in 2 wt% Yb³⁺-doped LuLiF₄ (LLF:Yb), measuring a cooling rate of 14.3 K/W near room temperature and predicting a minimum achievable temperature (MAT) of ~145 K based on the $\alpha = 4.2 \times 10^{-4} \text{ cm}^{-1}$ background absorption coefficient of the crystal.²²¹ LLF is an isomorph of YLF with the advantage of congruent melting and slightly lower phonon cut-off energy, however with the disadvantage of a greater

crystal-field splitting. Volpi *et al* have measured external quantum efficiencies (EQE) of >99% and $\alpha = 1.3 \times 10^{-3} \text{ cm}^{-1}$ in 5 wt% Yb^{3+} -doped LLF crystals.²²²

Figure 6-1. Laser cooling of YLF:Yb crystal: a) Cooling efficiency contour map evaluated for high purity YLF:10% Yb^{3+} crystal. b) Laser cooling experimental setup. The IPG pump laser providing >50 W at 1020 nm is isolated and combined with a Ti:Sapphire guide laser tuned to 1070 nm.

Comparing to rare earth doped counterpart, semiconductor has competitive advantage over lower cooling temperature achievable. Unlike in rare earth doped where the highest energy level of ground state is rapidly depopulated at low temperature due to Boltzmann statistics, charge carriers in direct bandgap semiconductor following Fermi-Dirac distribution sustain at much lower temperature.²²³⁻²²⁵ That is the reason why soon after the successful demonstration of laser cooling in rare-earth doped material in 1995, the research attention was directed to direct bandgap semiconductors. The initial attempt focused on GaAs and its hetero-structured materials due to their well-known high performance in photoluminescence quantum yield. Early theoretical work by A. N. Oraevskii in 1996 pointed out that for GaAs, the minimum photoluminescence quantum efficiency should be more than 98% in order to achieve laser cooling at room temperature.²²⁶ He also realized that it is impossible to achieve

this efficiency with pure GaAs due to large non-radiative recombination caused by surface defect. Thus, heterostructure of GaAs with a thin layer of InGaP₂ was chosen to study because in that sample, the surface recombination is suppressed. The first systematic and thorough experiment on laser cooling of GaAs/GaInP heterostructure was done by H. Gauck *et al* in 1997.²²⁷ In the experiment, a ZnSe hemisphere with a matched refractive index was used to improve the fluorescence extraction of the sample. The photoluminescence external quantum efficiency was measured using a bolometric thermal method where fractional heating of sample was recorded in accordance with different wavelength excitation. Even though an impressive external quantum efficiency of 96% was achieved in the sophisticated structure, no net cooling was observed. It was calculated that with the up-converted fluorescence of $1.4 k_B T$ achieved in GaAs/GaInP, a minimum of 97.5% external quantum efficiency is needed to obtain net cooling in the sample.

Early observation of net cooling of GaAs/AlGaAs multi-quantum wells heterostructure was reported by Finkeissen *et al* in 1999.¹⁵² The experiment was done at low temperature range (*i.e.*, 40-80K) with the excitation wavelength only ~ 10 meV below the fluorescence emission peak. By using an external magnetic field as an internal thermometer, the authors claimed to achieve maximum of 10% temperature drop from original starting temperature. However, this work was later pointed out by Hasselbeck *et al* in 2007 to be misinterpretation of fluorescence spectra which was shifted by Coulomb screening rather than temperature change.²²⁸

Later efforts on laser cooling of semiconductors mostly focused on synthesis and fabrication techniques to improve the external quantum efficiency of GaAs/GaInP hetero-structure. In 2004, M. Sheik-Bahae and R.I. Epstein theorized the laser cooling of semiconductor, particularly for GaAs case.²²⁹ In the paper, they mostly focused on

the photon absorption and recombination processes in semiconductors in which critical issues of luminescence trapping and red-shifting were considered for the first time in laser cooling research. They also discussed what are needed to be achieved experimentally in order to obtain net cooling in GaAs. From that, two main reasons that hindered the realization of net cooling in GaAs material were pointed out which are: internal reflectance and parasitic (background) absorption. The former reason is related to the external quantum efficiency of sample while the latter causes heating which could cancel any achievable net cooling in the sample. Thus, in order to observe net cooling experimentally, one not only has to achieve near unity external quantum efficiency but also to minimize the background absorption (or impurity absorption) of the sample. This judgement was strengthened by recent experiment with GaAs/GaInP double heterostructure carried by Bender *et al* (2013).²²³ In this experiment, the GaAs/GaInP structure was prepared using highly controlled metal organic chemical vapor deposition (MOCVD) technique. This resulted in double heterostructure of GaAs/GaInP where the lattice-matched cladding layers act both as surface passivation and carrier confinement. The sophisticated and carefully design of the structure with ZnS hemisphere made it possible to achieve a record high external quantum efficiency of 99.5% at 100 K as shown in Figure 6-2 below.²²³

Figure 6-2. All-optical scanning laser calorimetry data for GaAs/GaInP DHS performed at 100 K.

Even though the resulted EQE exceeded the requirement for obtaining laser cooling in GaAs/GaInP, no net cooling was observed experimentally. The high background absorption in the structure which caused heating was responsible for the positive temperature change. By fitting the parasitic absorption model introduced by M. Sheik-Bahae and R.I. Epstein, they was able to obtain a background absorption of 91 cm^{-1} which is much larger than calculated maximum tolerable background absorption of only 1.44 cm^{-1} in order to achieve net cooling.

Recently, successful demonstration of net laser cooling on high purity single crystal CdS nanobelt has been reported by Zhang *et al.*¹⁰³ This big achievement is an important milestone for laser cooling research community to re-visit other semiconductor materials. The case of CdS nanobelt, however, is an exception due to a near unity external quantum efficiency of the sub-wavelength thickness ($\sim 100 \text{ nm}$), in which the photon trapping and re-absorption is no longer an issue. Therefore, it is critical to find a suitable material with high external quantum efficiency and strong absorption

coefficient (*i.e.*, to minimize the background absorption) even in bulk form to realize net laser cooling for practical applications.

Lead halide perovskites have garnered tremendous attention in the past few years due to their high performance as light absorbers in solar cells^{1,17,95,230}, and optically pumped lasers²³¹⁻²³³. Recent work also shows that perovskite single crystals possess low trap-state density^{234,235} and high external quantum efficiency²³⁶, both of which are advantageous for laser cooling if a sufficient photoluminescence upconversion could be achieved. Interestingly, indeed we find that lead halide perovskite crystals in both 3D (*i.e.*, MAPbI₃) and 2D (*i.e.*, PhEPbI₄) forms show strong photoluminescence upconversion, suggesting the possibility of laser cooling as discussed in chapter 4. In this chapter, we will demonstrate experimentally that MAPbI₃ platelets grown by vapor phase synthesis and PhEPbI₄ samples exfoliated from a bulk crystal by solution synthesis can be laser cooled by ~23.0 K and 58.7 K, respectively, from room temperature.

6.2 Experiment method

6.2.1 Experiment setup and temperature measurement method

To precisely determine the local temperature at the sample upon laser cooling, we adopt a pump-probe luminescence thermometry (PPLT) technique, which is based on the sensitivity of the luminescence peak shifts when the local temperature of sample is changed. This technique is believed to be equivalent to the differential luminescence thermometry and is suitable for the laser cooling experiment if the cooling effect is significant. The pump-probe luminescence thermometry setup in our cooling experiment is shown in Figure 6-3. A cw Ti-sapphire laser with a tunable wavelength from 750 to 850 nm was used to pump in heating and cooling experiment while a solid

state 671 nm laser was used as a probe beam to measure the Stokes photoluminescence emission. The two lasers were collimated and focused thorough a 50× objective onto a single perovskite platelet. The shutter S_1 and S_2 were alternatively shut or opened to allow the transmission of the pump or probe lasers. In our cooling and heating experiments, after pumping for every 5 minutes, the shutter S_1 was blocked and S_2 was opened and the photoluminescence spectra were collected by a confocal triple grating spectrometer (Horiba-JY T64000) in a backscattering configuration using a liquid nitrogen cooled charge-coupled CCD detector. In order to prevent the heating effect of 671 nm laser, we kept the power as low as 13 μW and the collection integrating time of 1 second. The total time to obtain one PPLT spectrum is around 1 minute due to the time needed for spectrometer to move the gratings to cover the whole wavelength regime of interest.

Figure 6-3. (a) PPLT technique setup in laser cooling experiment; (b) A schematic diagram of the sample setup. Mica substrate is supported over two silicon pieces in order to further isolate sample from thermal dissipation. Then, whole sample is placed inside a cryostat which is vacuumed to 1×10^{-6} Torr.

The actual cooling setup was schematically shown in Figure 6-3b. The mica substrate (with the platelets) was peeled to be roughly 100 μm thin and was suspended between two supporters to minimize the thermal loss to the copper cold finger of the cryostat. Cryostat was maintained at $\sim 10^{-6}$ Torr during the experiment. The size of the

beam spot on the sample is $\sim 5 \times 5 \mu\text{m}^2$, which corresponds to a confocal pinhole of $\sim 500 \times 500 \mu\text{m}^2$ for the total signal throughput. To rule out other non-temperature dependent effects that can cause the band-shift in our laser cooling experiment, we have done a parallel control experiment with a good thermal contact of perovskite platelet crystals to the heat sink as shown in Figure 6-4.

Figure 6-4. Two configurations of sample setup: (1) Good thermal isolation setup; (2) good thermal contact setup.

This experiment was done with exactly the same platelet and laser excitation conditions. The result is shown in Figure 6-5 below. It clearly shows that the band edge emission shift (which indicates the laser cooling) was only observed in the configuration with good thermal isolation; while in the 2nd configuration the PL peak position remain almost the same during the experiment, suggesting the dominating heat dissipation to the heat sink. The result shows that the band edge emission shift of perovskite, which was used as a temperature indicator in our study, is temperature-dependent, and other non-temperature dependent effects can be ruled out at least in the condition of our laser cooling experiment.

Figure 6-5. PPLT spectra taken every 5 minutes for the same perovskite platelet (a, c) and spectra shift after 25 minutes of pumping by 785 nm at 0.7 mW (b, d) with different configurations of sample setup: (a), (b) With a good thermal isolation setup; and (c), (d) With a good thermal contact setup.

6.2.2 Photoluminescence versus temperature calibration in perovskites

Figure 6-6a and d show the temperature dependent photoluminescence spectra of MAPbI₃ and PhEPbI₄, respectively from 77 to 340 K, excited by a 671 nm laser for MAPbI₃ and 473 nm laser for PhEPbI₄ with a low power excitation (*i.e.*, 5-15 μ W) to minimize the heating effect. It is known that MAPbI₃ has an orthorhombic-to-tetragonal phase transition at ~ 150 K²³⁷. Our experimental results show that below 120 K, the photoluminescence peak at ~ 750 nm can be assigned to orthorhombic phase. From 120 K to 160 K, the perovskite exhibits a phase transition which leads to the appearance of a lower energy peak at ~ 780 nm (dashed box), which corresponds to the tetragonal

phase. From 160 K to 340 K, as temperature increases the PL peak linearly blue-shifts as illustrated in the inset to Figure 6-6a.

Figure 6-6. Optical characterizations of 3D (a, b, c) and 2D (d, e, f) perovskites, respectively. a, d: Normalized photoluminescence from 77 to 340 K. The inset is a temperature calibration curve extracted from temperature dependent photoluminescence data within the laser cooling experiment windows. b, e: Photoluminescence and the absorption spectra at 296 K. The green areas indicate possible cooling regime. c, f: Anti-Stokes photoluminescence (ASPL) spectra at 296 K. The inset to c displays the peak position and ASPL intensity versus pump power.

Based on this relationship, a temperature calibration curve can be obtained relative to the band edge emission at room temperature. It is important to note that the photoluminescence shift of the 3D perovskite is in opposite trend compared to conventional semiconductors, which will need further investigation for this material. Similar temperature calibration curve was also obtained for the 2D perovskite as shown in Figure 6-6d. It is important to note that the optical gap of 2D perovskite has similar trend versus temperature as traditional semiconductors. Figure 6-6b and e display the Stokes photoluminescence (red curve) taken at 296 K and the corresponding absorption spectra measured from the same crystal (black curve)²³⁸ for 3D and 2D perovskite,

respectively. The photoluminescence peak of 3D and 2D perovskites are at ~ 770 nm and 529 nm, respectively in good agreement with other reports²³⁹⁻²⁴². As moving to the band tail, the absorption decreases and reaches zero indicating that there should be no substantial phonon-assisted upconversion photoluminescence beyond this wavelength. The filled-green area under the absorption curve indicates possible cooling regime where the excitation photon energy is less than that of mean emission photoluminescence. Next, we investigate the intensity of the anti-Stokes photoluminescence (ASPL) *versus* laser power (Figure 6-6c and f). As shown in Figure 6-6c inset for 3D case, below certain excitation power, the ASPL intensity linearly depends on laser power indicating that phonon-assisted up-conversion process dominates. Above this power, ASPL intensity deviates from the linear dependence and even decreases if the laser irradiation sustains for a while, due to possible degradation at a high laser power. The blue-shift of ASPL peak above that critical power (inset to Figure 6-6c) indicates the heating of sample at higher excitation power (according to the calibration curve shown in Figure 6-6a). Therefore, in our laser cooling experiment, we limit the excitation power to be around 0.7 mW which is below the critical power to prevent heating of sample. We should comment that this upper-bound value of laser power varies from sample to sample, possibly due to the variations in crystalline quality and purity of samples. Further improvement in sample quality may improve critical power and thus laser cooling performance. As shown in Figure 6-6f for 2D perovskite, even at the excitation energy of 386 meV lower than the bandgap, the ASPL of 2D perovskite was still exceptionally strong. The power dependence ASPL (inset to Figure 6-6f) also indicates that the upconversion is a phonon-assisted process which is essential for realization of laser cooling in this material.

6.3 Laser cooling in $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet

6.3.1 Laser cooling results

To measure the cooling effect of the crystals, we adopt the pump-probe luminescence thermometry (PPLT) technique previously used in rare-earth materials and semiconductors²⁴³ as discussed in section 6.2.1. The mica substrate (less than 100 μm) having perovskite crystals was suspended to isolate the sample from the copper cold finger of the cryostat. Mica exhibits excellent transparency ($>95\%$ for 100 μm thick film at 770 nm)^{244,245}, low refractive index (~ 1.6) and thermal conductivity ($\sim 0.45\text{ W/m.K}$)²⁴⁶. Therefore, this design will reduce the background absorption, increase the luminescence extraction efficiency and reduce the thermal load during cooling experiment. Figure 6-7a and b display the evolution of photoluminescence spectra for two representative cooling and heating pumped at 785 nm and 760 nm, respectively. It is clearly seen that the photoluminescence red-shifts pumped by 785 nm, indicating a cooling process in the perovskite platelet (refers to the calibration curve shown in the inset to Figure 6-6a). On the contrary, 760 nm pumping leads to blue-shifted band edge, indicating a heating process.

After the pump lasers were turned off, the photoluminescence spectra returned to their original position indicating that the cooling-warming cycle is reversible. A summary of series cooling and heating experiments with different pumping wavelengths is shown in Figure 6-7c. The data show that the perovskite platelet crystals could be cooled by a maximum of $\sim 23.0\text{ K}$ from room temperature pumped by 785 nm with a power of 0.66 mW. The normalized cooling power density (in K/mW) is plotted in Figure 6-7d, showing a maximum cooling effect $\sim 35.0\text{ K/mW}$ around 780-785 nm, which is much larger than that in CdS nanobelts²⁴⁷.

Figure 6-7. Net laser cooling observation in 3D perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. a, Evolution of PPLT spectra starting from 296 K, pumped by a 785 nm laser with a power of 0.66 mW. b, Evolution of PPLT spectra starting from 290 K, pumped by a 760 nm laser with a power of 0.3 mW. c, Temperature change versus time pumped by eight laser lines using data extracted from the PPLT spectra. d, Summary of measured maximum ΔT (red filled-circles) and theoretically calculated temperature change (blue curve) normalized to pump power for different pump wavelengths at 296 K.

One possible explanation for such a big difference is the low thermal conductivity of perovskite materials²⁴⁸. The solid curve is a theoretical calculation based on Sheik Bahae-Epstein (SB-E) theory showing a reasonable agreement, except for the heating points (at 750 and 760 nm). This is understandable because perovskite is thermally unstable, especially under high vacuum (*i.e.*, 10^{-6} Torr). Thus, after long heating time, the sample may undergo degradation and affect the final local temperature.

6.3.2 Laser cooling origin in perovskite

To understand the excellent laser cooling properties in the perovskite crystals, we turn to the SB-E theory,²⁴⁹ which describes the net cooling power P_{net} in the semiconductor as:

$$P_{net} = \eta_e B N^2 (h\nu - h\bar{\nu}_f) + A N h\nu + C N^3 h\nu + \Delta P \quad (6-1)$$

where η_e is the extraction efficiency of the photoluminescence, N is the photo-excited electron-hole carrier density; A , B , C are the recombination coefficients of nonradiative (one particle), radiative (two particle), and Auger (three particle) processes, respectively; ν and $\bar{\nu}_f$ are excitation and mean emission luminescence photon frequency, respectively; and ΔP is a residual heating term accounting for free-carrier absorption and other parasitic absorptive processes, $\Delta P = \alpha_b I + \sigma_{fca} N I$, where α_b is the background absorption and σ_{fca} is the free-carrier absorption cross section and I is the laser irradiance intensity. This model excludes any possible two-photon process, which usually releases extra energy into lattice heat. When the excitation occurs near the band-edge, the interband absorption dominates and thus the term ΔP can be ignored. Then, the cooling efficiency could be expressed as:

$$\eta_c = \eta_{ext} \frac{\bar{\nu}_f}{\nu} - 1 = \left(\frac{\eta_e B N^2}{A N + \eta_e B N^2 + C N^3} \right) \frac{\bar{\nu}_f}{\nu} - 1 \quad (6-2)$$

here, $\eta_{ext} = \frac{\eta_e B N^2}{A N + \eta_e B N^2 + C N^3}$ represents the external quantum efficiency. The

cooling is possible when η_c is positive. The above phenomenological theory considers only free electron model, more discussions including excitonic effect, band-tail states and surface plasmon assisted laser cooling can be found in literature^{224,225,250,251}.

Based on equation (6-2), we plot the cooling efficiency as a function of external quantum efficiency η_{ext} and $\Delta E = h\bar{\nu}_f - h\nu$ for MAPbI₃ (band edge of 770 nm) shown in Figure 6-8a. As can be seen from the Figure, a minimal η_{ext} of ~ 0.95 and ~ 0.99 are required for excitation at 815 nm ($\Delta E = 95$ meV) and 780 nm ($\Delta E = 20$ meV), respectively, as indicated by the dashed lines. The cooling efficiency increases as the η_{ext} approaches unity. The calculation is valid only when the background and free-carrier absorption are negligible. As the excitation photon energy moves into the Urbach tail (*i.e.*, large ΔE), the interband absorption reduces dramatically and thus the background and free carrier absorption are no longer negligible.

Figure 6-8. Condition for laser cooling in CH₃NH₃PbI₃ platelets. a, Calculated cooling efficiency as a function of external quantum efficiency and energy difference between the excitation photon and emission photon energies b, Fractional heating (normalized with excitation power and absorption at the wavelength) for different sample thickness excited at higher band-gap wavelengths (750, 755, 760, 765 and 770 nm). The cross wavelength (λ_{cr}), which is the intersection between linear fitting line of fractional heating data and the x -axis at 0 fractional heating, will be used to calculate external quantum efficiency. c, External quantum efficiency of the perovskite platelets with different thicknesses calculated from b.

We then determine the external quantum efficiency of the perovskite platelets by using a bolometric calibration method which has been described in literature to measure external quantum efficiency of GaAs^{252,253}. The experimental setup is similar to our

laser cooling experiment described above. We used various laser wavelengths with energies higher than that of the mean emission photoluminescence of perovskite platelets to pump and record the temperature change in the samples. The excitation power for different wavelengths was adjusted so that the emission photoluminescence intensity in each experiment is comparable. This is to ensure that the total emitted photons for each wavelength are constant considering the photoluminescence collection efficiency of our optical system remained unchanged in all measurement. In addition, the excitation powers should be kept low enough (*i.e.*, <0.1 mW) to avoid heating of sample which may affect the local temperature. Figure 6-8b shows the fractional heating at various wavelength excitations for four different thicknesses. From this result, we can determine the λ_{cr} which is the intersection between the linear fit of the fractional heating at different wavelength and the x -axis. This was then used to calculate the external quantum efficiency of the perovskite platelet as shown in Figure 6-8c. As we can see, the external quantum efficiency is extremely high for those perovskite platelets and reaches maximum at the thickness around 1.5 μm . This high value of external quantum efficiency (*i.e.*, $\sim 99.8\%$) explains why we could observe net laser cooling even with excitation wavelength at 780 nm where the minimal external quantum efficiency required for cooling is 99% (Figure 6-8a).

6.3.3 Thickness dependence cooling

To further elaborate this, we conducted thickness-dependent cooling on a variety of platelet crystals. Figure 6-9a shows anti-Stokes photoluminescence spectra of perovskite platelets with different thicknesses. As seen from Figure 6-9b, the mean emission luminescence peak red-shifts as thickness increases. The absorption spectrum of individual platelets reveals that the band edges are nearly the same with different

thicknesses (Figure 6-9c). Therefore, the mean emission luminescence peak shift is not due to the difference in band edge but may stem from other reasons such as surface depletion²⁴⁷ which should be further studied. Nevertheless, based on the data, we can calculate ΔE of different thickness regard to excitation wavelength 785 nm.

Figure 6-9. Anti-Stokes luminescence dependence on thickness of perovskite platelets. (a) ASPL spectra of perovskite platelets at different thickness. The excitation wavelength and power are 785 nm and 70 μW , respectively. (b) Mean emission luminescence peak position and intensity dependence on thickness extracted from a. (c) Absorption spectra of individual platelets with different thickness measured by microspectrophotometer (CRAIC-20). d, Thickness dependence of energy difference ΔE (upper), cooling efficiency η_c (middle), and calculated cooling power P_c (lower). The calculated cooling powers for different thickness are in good agreement with experimental results of net cooling (red filled-circle).

Figure 6-9d summarizes the thickness dependent ΔE (upper panel), calculated cooling efficiency (middle panel) and calculated cooling power by the 785 nm excitation (lower panel). The cooling power of perovskite platelets with different

thicknesses was estimated based on the actual absorption measured. We note that the trend of the calculated cooling power versus thickness agrees with the experimental values in K/mW. The maximal cooling of 8.8 μW can be achieved at a thickness ~ 2.0 μm , in agreement with our experimental observation as well. The estimated blackbody radiation is ~ 2.0 nW, therefore the thermal conductive heat dissipation dominates.

6.4 Laser cooling in 2D perovskite single crystal

6.4.1 Laser cooling results

Similar cooling experiment was carried out for 2D perovskite and the results are summarized in Figure 6-10.

Figure 6-10. Net laser cooling observation in 2D perovskite ($\text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{NH}_3$)₂PbI₄. a, Evolution of PPLT spectra starting from 296 K, pumped by a 543 nm laser. The pump laser was turned on again to show that the cooling and warming process were fully reversible. b, The peak position and FWHM extracted from PPLT spectra during laser cooling and warming processes show that both of them follow the temperature calibration curve. c, Temperature change versus time pumped by six lasers (473, 502,

514, 532, 543, and 565 nm), using data extracted from the PPLT spectra. d, Summary of measured maximum ΔT (red-filled-circles) and theoretically calculated temperature change (blue curve) normalized to pump power for different pump wavelengths at 296 K.

Figure 6-10a shows the PPLT spectra of cooling-warming-cooling cycle starting from 296 K pumped by 543 nm laser. As we can see, whenever the pumping laser was on, the PPLT spectrum was blue-shifted indicating cooling of the crystal. This experiment shows that the cooling and warming process is reversible and reproducible as well. Figure 6-10b shows the evolution of photoluminescence peak and full width at half maximum (FWHM) of the spectra extracted from Figure 6-10a for the first cooling-warming cycle. It is noted that both photoluminescence peak position and FWHM evolutions are in good agreement with the calibration curve shown in Figure 6-6d for the 2D perovskite. This is strong evidence that the sample is indeed cooled down by the pump laser. Figure 6-10c and d summarize the cooling and heating of 2D perovskite crystal by various wavelength laser pumping. The maximum cooling of 58.7 K directly from room temperature was achieved with 565 nm laser excitation. The cooling and heating results also agree well with the calculation based on SB-E theory as shown in Figure 6-10d.

6.4.2 Cooling of a thermal load on perovskite crystal

To further elaborate the cooling of 2D perovskite crystal, we designed a macroscopic optical cooler using the 2D perovskite crystal to cool an external thermal load of CdSe nanobelts, reminiscent of a microscopic CdS solid state optical cooler²⁵⁴. The experimental setup is schematically shown in Figure 6-11a. CdSe nanobelt grown by chemical vapor deposition method was used as a temperature probe (hence thermal load) for the cooling experiment. The nanobelts with a thickness of ~100 nm, width of

2-4 μm , and length of $\sim 10 \mu\text{m}$ have been placed on top of a mechanically exfoliated 2D perovskite crystal sheet (inset to Figure 6-11a) which is supported by two SiO_2 bars for thermal isolation. The whole setup was placed inside a cryostat which was then pumped down to 10^{-6} Torr to prevent environmentally thermal conduction. In this experiment we used only one laser (*i.e.*, 543 nm) to pump 2D perovskite to induce laser cooling while simultaneously the same laser is used to probe the photoluminescence of CdSe nanobelt which has a peak position around 710 nm as a temperature indicator.

Figure 6-11. A macroscopic 2D perovskite optical cooler cooling a CdSe nanobelt thermal load. a, Experimental setup: CdSe nanobelt with a thickness of ~ 100 nm, width of ~ 2 -4 μm and length of $\sim 10 \mu\text{m}$ were placed on top of an exfoliated 2D perovskite sample. The 543 nm pump laser was used to excite the 2D perovskite area near the nanobelt. The inset at right corner displays an optical image of CdSe nanobelts laid on top of 2D perovskite sample. b, Evolution of PPLT spectra starting from 296 K which show a blue-shift of 2.76 nm after 10 minute pumping indicating a cooling of 28 K (inset). c, Temperature calibration curves for 5 different CdSe nanobelts.

The temperature calibration curve extracted from temperature dependent photoluminescence for the CdSe nanobelt was done separately as shown in Figure 6-11c. The laser spot was positioned nearby the edge of the nanobelt so that the cooling of CdSe nanobelt by 2D perovskite crystal is maximized. The PPLT spectra evolution of CdSe during the cooling experiment is shown in Figure 6-11b. Based on the temperature calibration curve (Figure 6-11c), the CdSe nanobelt was observed to be cooled by ~ 28.0 K from room temperature. It is noted that the cooling result for CdSe nanobelt is lower than the 2D perovskite itself as shown in Figure 6-10a and c (*i.e.*, ~ 52 K) for the same excitation condition. This is probably in part due to the heating effect caused by the absorption of CdSe nanobelt for the 543 nm wavelength, as well as the thermal conductive loss due to the nanobelt.

6.5 Discussion

Perovskite material are gradually outperforming traditional semiconductors in many opto-electronic applications. It has been considered as the fastest developed solar cell material in the history. The recent record on solar cell efficiency already approach that of crystalline silicon. For a low cost, low temperature process material like perovskite, many mysterious questions still remain for research community. The origin of strong electron (exciton)-phonon coupling and abnormal bandgap shift in both 2D and 3D perovskite are still in debate. For laser cooling application, one of the remained questions is how to scale this material and to apply in a physical cooling device with suitable heat sink design. This engineering question may face a big challenge due to the nature low thermal conductivity of the perovskite. The preparation method play an important role in the quality of perovskite. There have been reports on multiple defect peaks in both 2D and 3D perovskite (Figure 6-12a-c) which are caused by impurities

during the synthesis.²¹⁵ In order to successfully achieve net cooling, these defect peaks should be eliminated completely. Figure 6-12d and e are photoluminescence spectra of 2D perovskite at 78K prepared by conventional method and our controlled method, respectively. It is clearly seen that with the highly controlled process, the long wavelength defect peak can be suppressed. However, even with carefully experimentation, the quality of the perovskite crystal can vary from batch to batch and not every time we can realize net laser cooling. It is important to note that, in order to achieve net cooling, the required external quantum efficiency in perovskite must be at least 98%. Thus a small difference in sample quality can prevent the realization of net cooling.

Figure 15. Defect state in lead halide perovskites. a-c, trap states in 2D perovskite revealed by transition absorption and photoluminescence measurement. d,e. Photoluminescence measurement at 78 K of spincoated (d) and single crystal (e) sample.

Another challenge in perovskite material is its stability. This challenge is not only laser cooling research but also in other opto-electronic applications of the material. It is well-known that the perovskite material is unstable to both surrounding environment

agents such as moisture or oxygen and illumination of light. This challenge is the biggest barrier that hinders the perovskite material from commercial applications. However, the research community is actively resolving this problem together. By either replacing the organic component in perovskite formula or combining 2D and 3D perovskite or using a protecting layer on the surface of 3D perovskite, the stability of this material can be enhanced significantly.^{3,28,31} Recent results on stable perovskite solar cell devices make great promise to the use of this material in practical applications in near future.

6.6 Summary

We have demonstrated laser cooling of both 2D and 3D lead halide perovskite materials. The maximum cooling of 23.0 K and 58.7 K has been achieved for the MAPbI_3 and PhEPbI_4 perovskites, respectively. We have also demonstrated an actual perovskite optical cooler in which a CdSe nanobelt can be cooled by 28.0 K from room temperature. Our work expands the toolbox for optical refrigeration extensively, considering the numerous combinations of inorganic-organic perovskites. With the facile solution processing and accessible crystallization temperature of those perovskite materials, our work opens up the possibility of laser cooling devices facily bonded to electronic and optoelectronic thermal load. The remaining challenges are to scale up the current vapor phase or solution synthesis towards a uniform macroscale crystalline film and the proper design of the heat sink, since the thermal conductivity of those perovskites is usually low.

Chapter 7: Conclusions and future works

7.1 Conclusions

In this dissertation, the synthesis of high quality single crystal lead halide perovskites and the investigation of their excellent optical properties are the main focus. The controlled growth using chemical vapor deposition (in the case of 3D perovskite) and solution-based crystallization (in the case of 2D perovskite) is responsible for superior optical characteristics of our samples comparing to conventional preparation methods. These properties include: long carrier diffusion length, strong photoluminescence, lack of defect state, and strong electron/exciton –phonon coupling (*i.e.*, leading to strong phonon-assisted upconversion photoluminescence).

I have developed a two-step growth technique of high quality 3D perovskite crystal using a home-built chemical vapor deposition system. The method includes the growth of single crystal lead halides on a substrate and a vapor-solid hetero-phase intercalation step to convert them into respective perovskite. The substrate that I chose is muscovite mica which is a layered material with super flat surface. The substrate promotes the growth of crystal in horizontal direction due to the lattice matching between the two. By using this method, I were able to grow well-defined single crystal perovskite nanoplatelets and nanowires. Because in the synthesis only high purity precursor (*i.e.*, 99.999%) and inert gas were used, the resulted crystals showed very high quality both in term of crystallinity and optical properties. I have also developed a single-solvent solution based crystallization technique to grow single crystal 2D perovskite. The crystal can be grown in millimeter size with super high purity. Then, a conventional Scotch-tape mechanical exfoliation was used to prepare high quality 2D perovskite flake with suitable thickness for optical study.

To prove the high quality of the grown crystals, the carrier diffusion length was measured and compared with previously reported value. I have used the same method of measurement in the literature for the perovskite using time-resolved photoluminescence technique and a carrier quenching layer such as: PCBM.²³⁰ The result showed that the crystal grown by my method has twice the carrier diffusion length as that of sample prepared by conventional spin-coating method. It is noted that the carrier diffusion length is an important characteristic of the material in various applications such as: solar cell, light emitting diode, *etc.* It implies that the defect density or trapping sites in my perovskite crystal is much less than that prepared by solution method. This conclusion is strengthened by the result of low temperature photoluminescence measurement where defect states can be clearly seen at the longer wavelength in solution-prepared sample while no detectable defect peak is observed in my single crystal perovskite.

I also observed the phase-transition in the 3D perovskite crystal by using temperature-dependent photoluminescence spectroscopy which agreed well with previous study using temperature dependent XRD. From this, photoluminescence characteristic of each phase was assigned and the phase transition temperature range was investigated. Another important observation is the abnormal bandgap shift in the perovskite comparing to conventional semiconductor. I chose $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite to investigate in detail as a case study. Although the origin of this phenomenon is still in debate, I believe the reason for this is the strong electron/exciton – phonon interaction in the perovskite. One of the reason is that: the bandgap of semiconductor thermally depends on two factors: lattice expansion and electron-phonon coupling. Since the lattice expansion of perovskite has been previously studied which showed a positive correlation (*i.e.*, similar to conventional semiconductor), the reason for the abnormal

shift must be from electron-phonon coupling. Another reason is that we discovered a very strong phonon-assisted upconversion photoluminescence in perovskites. This is caused by the strong electron/exciton-phonon interaction. This is the first time the phonon-assisted upconversion photoluminescence of perovskite was investigated and this turned out to be the key element in the experiment realizing the net laser cooling of this material.

Lead halide perovskites are famous for their excellent optical absorption and luminescence emission properties. It was expected that it is also a good gain material for stimulated emission application. The optically pumped lasing of perovskite nanoplatelets in this thesis is among the very first report on laser application for this material. Surprisingly, the single crystal platelet can act as a naturally formed whisper gallery mode cavity to confine and amplify the photoluminescence. The lasing quality in this crystal is comparable with the one using external DBR cavity for the same material which was reported at almost the same time with my paper.⁵³ The advantage of using perovskite as lasing material is the ease of tuning emission wavelength from UV to near IR simply by changing the halogen composition. Another interesting finding is that I were able to achieve lasing in 2D and 2D-3D perovskites which were previously thought impossible to achieve.²¹⁴ By using just exfoliated flake from single crystal 2D perovskite, optically pumped lasing can be achieved at low temperature (*i.e.*, 78 - 200K). This was attributed to the lack of defect state and longer carrier lifetime in my 2D perovskite crystal comparing to the one reported in literature.

Laser cooling of semiconductor requires very strict conditions of the sample such as: super high purity (*i.e.*, to minimize back ground absorption), near unity external quantum efficiency, and most importantly, strong phonon-assisted upconversion photoluminescence. As previously discussed, I discovered a very strong phonon-

assisted upconversion photoluminescence in both 2D and 3D perovskites. By carefully preparing high purity samples and designing experiment, I were able to demonstrate net laser cooling in the material right from room temperature. A prototype cryo-cooler using 2D perovskite crystal to cool a CdSe nanobelt was also demonstrated. The large temperature difference detected in the cooling experiment (*i.e.*, ~58K) may be in part due to the very low thermal conductivity of the material. Nevertheless, the discovery of the laser cooling phenomenon in this family of material may push the field forward in finding suitable material for practical laser cooling applications even though some critical issues such as low thermal conductivity and stability are needed to be addressed beforehand.

7.2 Future works

There are two trends now in the perovskite research: The first one is to improve the performance of perovskite devices (*i.e.*, solar cell, LED) by using different approaches of synthesis and design of material, the other one is to explore fundamental properties of perovskite and its new applications in other optoelectronic devices. 2D and 2D-3D hybrid perovskite has not been given much attention and there are a lot of interesting things to be investigated for this material class. In the optical point of view, the 2D perovskite with multiple quantum well structure formed by the organic and lead halide octahedron layers is an interesting subject to study matter-light interaction, quantum confinement, exciton-phonon coupling, *etc.* I believe that in the next few years, the perovskite research community will gradually shift their interest in the 2D and 2D-3D perovskites. Thus, there are few un-finished stories that I would like to follow in the near future of my research which will be presented here with some preliminary data.

Exciton-phonon interaction in 2D perovskite

Even though exciton-phonon interaction in 2D perovskite is expected to be strong, there is still lack of systematic study on this matter. One of the main reason that the laser cooling can be achieved in this material is because of its super strong phonon-assisted upconversion photoluminescence even with the pumping wavelength of ~ 390 meV below the bandgap as discussed in Chapter 4 and 6. Thus, it must have the strong exciton-phonon coupling. However, how the interaction behaves at different temperature and different crystallinity is unknown. Figure 7-1 below shows the temperature dependent photoluminescence of PhEPbI₄ 2D perovskite single crystal.

Figure 7-1. Temperature dependent photoluminescence of 2D perovskite: PhEPbI₄. (a) Photoluminescence spectra in the range of 295 – 78 K showing blue-shift of PL peak. (b) Photoluminescence spectra in the range of 100 K – 9.5 K showing red-shift of PL peak. (c) Peak position and FWHM extracted from spectra in (a) and (b).

It is noted that the “V-line” shape of peak position versus temperature curve which shows the transition at around 100 K. Is this transition is caused by the weaker exciton-phonon interaction at lower temperature? Another question is the change in intensity at 20 K and the appearance of shadow peak which may be attributed to phonon-replica as shown in Figure 7-2.

Figure 7-2. Temperature dependent photoluminescence at sub-50 K temperature. (a) Photoluminescence spectra evolution from 50 K – 9.5 K. (b) The appearance of S2 peak which may be attributed to phonon-replica. (c) Photoluminescence intensity change from 50 – 9.5 K. (d) Peak position and FWHM extracted from spectra in (a).

Interestingly, I found out that the abnormal behavior of photoluminescence spectra (*i.e.*, “V-line” shape) is dependent on the crystal quality of the sample. I have prepared the 2D perovskite by 3 different methods: solution growth (single crystal), CVD growth (polycrystalline), and solution spin-coating. The temperature dependent photoluminescence result is shown in Figure 7-3.

Figure 7-3. Abnormal temperature-dependent photoluminescence in 2D perovskite PhEPbI₄ prepared by three different methods: solution growth (single crystal); CVD-grown; and solution spincoating.

As we can see that, in the single crystal, the transition temperature is around 100 K while that of CVD-grown sample is around 200 K. The spincoating sample, however, there is only blue-shift behavior which is the same trend with single crystal at low temperature. The result for spincoating sample also agrees with previous report on temperature dependent photoluminescence of the material. I suspect that the strong exciton-phonon interaction in the 2D perovskite is the reason to cause the red-shift at higher temperature. The higher crystallinity of sample, the stronger exciton-phonon interaction. However, more experiments are needed to be done to verify this conclusion. I also observed similar phenomenon in other 2D perovskite with different organic group such as: Tert-butyl-PbI₄, Butyl-PbI₄, and 2-Ethyl-N-Butyl-PbI₄ as shown in Figure 7-4. This means that the phenomenon is universal in 2D perovskite family, not just particular PhEPbI₄.

Figure 7-4. Temperature dependent photoluminescence of several 2D perovskites: Tert-Butyl-PbI₄, Butyl-PbI₄, and 2-Ethyl-N-Butyl-PbI₄.

If we can understand the exciton-phonon interaction, we can understand how the phonon-assisted upconversion photoluminescence is so strong in this type of material which leads to the experimental demonstration of laser cooling. From this study, we can also explore the dependence of crystalline quality on the exciton-phonon interaction and thus, other optical properties.

Raman spectroscopy study in 2D perovskites

Related to the phonon in the 2D perovskite crystal, it is important to understand the vibrational modes in the Raman spectra of 2D perovskites. This work requires both theoretical calculation and experiment using Raman Spectroscopy. I have done temperature dependence Raman of PhEPbI₄ perovskite using non-resonance excitation condition as illustrated in Figure 7-5.

Figure 7-5. Temperature dependence Raman spectra of PhEPbI₄ perovskite. (a) Low frequency temperature dependence Raman spectra from 80 – 290K. (b) Zoom-in spectra for N4 – N7 peaks. (c) Zoom-in spectra for N1- N4 peaks.

The nature of the peaks (*i.e.*, vibrational modes: shearing mode, breathing mode, *etc.*) is not well-understood and needed to determine by both theoretical calculation and other related experiments such as: polarization Raman, thickness-dependence Raman, *etc.* Thus, I just labeled the observed peaks as N1-N7. Some of the trends can be observed from the Raman data above such as: The abrupt shift of peaks N5, N6, N7 and the splitting of N4 at below 100 K, the increasing of relative intensity of N1 at lower temperature, most of the peaks are blue-shifted at lower temperature. To resolve more vibrational modes, I conducted the temperature dependence Raman experiment at even lower temperature down to 10 K, especially focusing on the profound peaks N1-N3. The result is shown in Figure 7-6 below.

Figure 7-6. Temperature dependence Raman spectra of PhEPbI₄ down to 10 K.

As we can see, at very low temperature (*i.e.*, < 50K), there are appearance of side-peaks next to all N1-N3 peaks. The splitting evolution is very clear for peak N2 and N3. It is interesting to note that, even at temperature as low as 10 K, the phonon vibrations of the perovskite is still very strong unlike most of conventional semiconductors. However, more experiments are needed to systematically study the Raman spectra of the material as well as the theoretical calculation to understand the origin of the above peaks.

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Publication List

Journal Publications:

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5. Jun Xing, Xinfeng Liu, Qing Zhang, **Son Tung Ha**, Yanwen Yuan, Chao Shen, Tze Chien Sum and Qihua Xiong, "Vapor Phase Synthesis of Organometal Halide Perovskite Nanowires for Tunable Room-Temperature Nanolasers", *Nano Lett.* 15(7), 4571 - 4577 (2015).
6. **Son Tung Ha**, Xinfeng Liu, Qing Zhang, David Giovanni, Tze Chien Sum and Qihua Xiong, “Synthesis of organic-inorganic lead halide perovskite nano-platelets: Towards high performance perovskite solar cells and opto-electronic devices”. *Adv. Opt. Mater.* 2, 838-844 (2014) (*Highlighted as the Frontispiece*)
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9. M. Iqbal Bakti Utama, Xin Lu, Da Zhan, **Son Tung Ha**, Yanwen Yuan, Zexiang Shen, and Qihua Xiong, “Etchantless patterning method on 2D materials for electronic characterizations and applications of CVD-grown MoSe_2 ”. *Nanoscale*. 6(21), 12376-12382 (2014)

Patent application:

1. Qihua Xiong, **Son-Tung Ha**, Chao Shen, Jun Zhang, “Laser cooling of lead halide perovskites”, US patent application, US20160109167 A1 (2016).