Temperature dependent spectroscopic studies of all-inorganic lead halide perovskites : towards efficient and stable optoelectronic applications

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**TEMPERATURE DEPENDENT SPECTROSCOPIC STUDIES
OF ALL-INORGANIC LEAD HALIDE PEROVSKITES:
TOWARDS EFFICIENT AND STABLE OPTOELECTRONIC
APPLICATIONS**

CHEN XIAOXUAN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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CHEN XIAOXUAN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 3 is published as Xiaoxuan Chen, Yue Wang, Jizhong Song, Xiaoming Li, Jiayue Xu, Haibo Zeng and Handong Sun. “Temperature Dependent Reflectance and Ellipsometry Studies on a CsPbBr₃ Single Crystal.” *J. Phys. Chem. C* **2019**, 123 (16), 10564-10570. DOI: 10.1021/acs.jpcc.9b01406

The contributions of the co-authors are as follows:

- Prof Sun guided the project direction, improved the manuscript draft, and gave valuable advices.
- I prepared the manuscript draft. The manuscript was revised by Prof Sun and Prof Wang.
- I co-designed the study with Prof Sun and performed all the laboratory work at the school of physical and mathematical sciences. I also analyzed the experimental data.
- The sample is provided by Prof Song, Prof Xu and Prof Zeng.
- Prof Zeng and Prof Li gave suggestions about the manuscript.

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The contributions of the co-authors are as follows:

- Prof Sun provided the platform for long-distance cooperation and guided the project direction.
- Prof Wang, Y. prepared the manuscript draft. The manuscript was revised by Prof Sun.
- I assisted in the optical characterization of the nanocomposites, data analysis and interpretation of the results.

- Dr. Wang, Z. helped to fabricate the device.
- Dr. Yu, Prof Li, and Prof Zeng provided the sample.
- Prof Zeng and Dr. Nalla gave suggestions about the manuscript.

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Abstract

Lead halide perovskites have attracted enormous interest for their excellent optoelectronic properties like the long carrier diffusion length, high quantum yield, bipolar charge carrier transport, high absorption coefficient, convenient spectral tunability, etc. They are promising candidates for next-generation solar cells, optically pumped lasers, light-emitting diodes, and photodetectors. However, the most widely studied organic-inorganic hybrid lead halide perovskites suffer from instability during shelf storage as well as under operation conditions. All-inorganic perovskites are alternatives that present better stability and competitive performance. With the impetus to delve into this less-explored material system and accelerate the development of all-inorganic lead halide perovskites towards optoelectronics with high efficiency and stability, I have carried out systematic spectroscopic studies with temperature assessment. I began with temperature-dependent reflection spectroscopy from 10 K to 300 K to investigate the intrinsic properties of Wannier-Mott excitons in CsPbBr₃ single crystals. The exciton-phonon interaction, exciton polaritons, and oscillator strength were revealed together with the wavelength-dependent dielectric constants, absorption cross-section, optical conductivity, and dispersion relation. These explain the exceptional optical properties of all-inorganic lead halide perovskites and show great prospects for possible optoelectronic applications. Next, to tackle the challenge of temperature-shifted lasing that commonly exists in conventional semiconductors, CsPbBr₃ perovskite nanocrystals were incorporated in the Cs₄PbBr₆ host matrix and demonstrated temperature-insensitive stimulated emission spectrum under two-photon pumping from 20 °C to 150 °C. Last but not least, I examined the thermal stability of CsPbBr₃ perovskites under higher temperature (>150 °C) with in-situ ellipsometry to monitor the annealing and degradation

process. CsPbBr_3 exhibited an upper limit of thermal stability of 250 °C (in UHV), due to the irreversible process of lead halide sublimation. Moreover, a hybrid structure of CsPbBr_3 as the active material and CsPb_2Br_5 (from water-assisted phase conversion) as heat and water barrier is proposed, which provides insights towards stable and efficient optoelectronic applications.

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List of Publications

- [1] Zitong Zhang, Yi Tian Thung, Xiaoxuan Chen, Lin Wang, Weijun Fan, Lu Ding, and Handong Sun. *Study of Complex Optical Constants of Neat Cadmium Selenide Nanoplatelets Thin Films by Spectroscopic Ellipsometry*. **The Journal of Physical Chemistry Letters** 2020, 12 (1), 191-198.
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- [3] Xiaoxuan Chen, Shijia Cheng, Lian Xiao and Handong Sun. *Identifying, Understanding and Controlling Defects and Traps in Halide Perovskites for Optoelectronic Devices: A Review*. **Journal of Physics D: Applied Physics** 2020, 53 (37), 373001.
- [4] Xiaoxuan Chen, Yue Wang, Jizhong Song, Xiaoming Li, Jiayue Xu, Haibo Zeng and Handong Sun. *Temperature Dependent Reflectance and Ellipsometry Studies on a CsPbBr₃ Single Crystal*. **The Journal of Physical Chemistry C** 2019, 123 (16), 10564
- [5] Xiaoxuan Chen, Shijia Cheng and Handong Sun. *Unraveling the Temperature Dependent Interband Transitions, Intrinsic Exciton Resonances and Complex Dielectric Constants of All-inorganic Perovskites for Next-generation Optoelectronics*. **OSA International Photonics and OptoElectronics Meeting** 2019 OW3D.7.
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- [9] Yue Wang, Dejian Yu, Zeng Wang, Xiaoming Li, Xiaoxuan Chen, Venkatram Nalla, Haibo Zeng and Handong Sun. *Solution-Grown $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ Perovskite Nanocomposites: Toward Temperature-Insensitive Optical Gain*. **Small** 2017, 13 (34), 1701587.

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Chapter 1

Introduction

In this chapter, a literature review of all-inorganic halide perovskites will be presented, including crystal structures, synthesis methods, basic optical properties, and possible light emission and emitting devices. Following that, I will give the outline of this dissertation focused on this kind of intriguing material and its potential applications.

1.1 ALL-INORGANIC HALIDE PEROVSKITES

Halide perovskites has drawn enormous attention in recent years as a promising candidate for next-generation optoelectronics. The efficiency of halide perovskite-based solar cells, for instance, has soared from 3.8% to 25.2% in a decade,¹⁻² owing to the high absorption coefficient ($10^4 \sim 10^5 \text{ cm}^{-1}$), long charge carrier diffusion length ($>1 \text{ }\mu\text{m}$), ambipolar carrier transport ($m_e^* \approx m_h^* \sim 0.2m_0$) and high mobility ($1 \sim 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) of this kind of material.³⁻⁸

However, to realize commercialization, the stability of halide perovskites must be improved. The most widely investigated organic-inorganic hybrid halide perovskites suffer from the instability of the organic cation which can be easily evaporated at 80 degrees Celsius,⁹ leading to decomposition of the perovskite structure. By the *International Electrotechnical Commission IEC61215:2016*, the photovoltaic stability should at least reach the standard of 1000 h under 85 degrees Celsius and 85% relative humidity. Moreover, the organic-inorganic hybrid halide perovskites can easily degrade under light irradiation and light-induced phase segregation.¹⁰⁻¹³ All-inorganic halide perovskites were then developed by replacing the organic cations with inorganic ones, and they have shown better stability and competitive performances.¹⁴ In the following sections, we will discuss the crystal structure, synthesis method, basic optoelectronic properties, and viable applications of all-inorganic halide perovskites.

1.1.1 Composition and Crystal Structure

Perovskites are a group of materials that have a similar crystal structure as calcium titanium oxide (CaTiO_3). It is named after the Russian mineralogist L. A. Perovski. The general chemical formula for perovskites is ABX_3 . For halide perovskites, A stands for monovalent cation such as methylammonium CH_3NH_3^+ (MA^+), Cesium/Caesium (Cs^+), Rubidium (Rb^+),

formamidinium $\text{CH}_3(\text{NH}_2)_2^+$ (FA^+). B ion is the bivalent cation which can be lead (Pb^{2+}), tin (Sn^{2+}), and germanium (Ge^{2+}). X stands for the halogen anion including chlorine (Cl^-), bromine (Br^-), and iodine (I^-) element.¹⁵ If A cation is MA^+ or FA^+ , then the perovskite will be a hybrid organic-inorganic halide perovskite, and if A cation is Cs^+ or Rb^+ , then it becomes an all-inorganic one. In this introduction as well as the subsequent parts of this thesis dissertation, the latter one is under our focus for most of the time.

FIG. 1.1 a) The schematic structure of halide perovskites with either inorganic or organic monovalent cations. b) Tolerance factor t and octahedral factor μ of different combinations of elements. Reproduced with permission.¹⁶ Copyright 2019, Elsevier.

From figure 1.1 (a), we can see that a typical halide perovskite structure consists of corner-joined $[\text{BX}_6]^{4-}$ octahedra and A^+ cations that fill the cage formed by the surrounding octahedra. The stability of the three-dimensional perovskite structure depends on the relative sizes of the component elements. The Goldschmidt tolerance factor (t) is described as

$$t = \frac{R_A + R_B}{\sqrt{2}(R_B + R_X)} \quad (1.1)$$

where R_A , R_B , and R_X are the effective radii of A, B, and X atoms respectively.¹⁷⁻¹⁸ To maintain a perovskite structure, t should be between 0.813 and 1.107 in general.¹⁹

The electronic band structures near the band edges are dominated by the $[\text{BX}_6]^{4-}$ octahedrons. The octahedral factor μ is used to evaluate the stability of the octahedrons,

$$\mu = \frac{R_B}{R_X}, \quad (1.2)$$

and μ should be a value between 0.442 to 0.895.¹⁹ The values of tolerance factor t and octahedral factor μ of different combinations of elements are summarized and mapped in figure 1.1 (b).

all-inorganic halide perovskites have different crystal structures including cubic (α), tetragonal (β) structure, and orthorhombic (γ) structures depending on the temperature, pressure, and composition. For CsPbCl_3 , the phase transition occurs at 42 °C (from orthorhombic to tetragonal) and 47 °C (from tetragonal to cubic).²⁰ For CsPbBr_3 , the two phase transitions occur at 88 °C and 130 °C respectively.²¹⁻²² For CsPbI_3 , the typical temperatures for phase changes are 175 °C and 260 °C (or above 310 °C).²³⁻²⁴ At room temperature, there is a great chance for black phase CsPbI_3 to turn into a non-perovskite structure yellow phase $\delta\text{-CsPbI}_3$, which changes its color from black to yellow due to the appreciable alteration of the bandgap (from 1.73 eV to 2.82 eV) induced the phase change. The clear difference between the yellow and black phase is demonstrated in figure 1.2.

FIG. 1.2 Structural phase transitions of CsPbI_3 . Upon heating, a) non-perovskite yellow phase CsPbI_3 can be converted back into the desired b) cubic black phase. c) During cooling, the tilting angle between the octahedrons increases from cubic to tetragonal and from tetragonal to orthorhombic phase. Atomic structures are sketched with blue atoms indicating Cs atoms, purple ones indicating I atoms, and green ones indicating Pb atoms. Reproduced with permission.²³ Copyright 2018, American Chemical Society.

The contrastive electronegativity between the Pb ions and the Halogen ions makes the chemical bonds short and ionic.²⁵ On the one hand, the soft and ionic nature of CsPbX_3 can induce ion migration, phase separation, and vacancy formation.²⁶ On the other hand, it makes the synthesis of CsPbX_3 much more facile. Compared to metal chalcogenide which has a covalent bond, the temperature required for preparing all-inorganic halide perovskites is much lower owing to ionic metathesis reaction.²⁷ The ionic lattice of CsPbX_3 also facilitate the ion

exchange of halogen atoms, which is beneficial for bandgap tuning and multicolor emission. We will discuss this in detail in the next section.

1.1.2 Synthesis Methods

The synthesis method of all-inorganic halide perovskite can be categorized into two kinds in general, including solution processing method or physical vapor deposition method. Each kind has its own advantages and limitations. Solution processing is considered to be more cost-effective, but the homogeneousness and reproducibility is difficult to control. While the physical vapor deposition is more complex, expensive, and energy-consuming, the crystallinity and the surface smoothness of the material can be enhanced with the right growth parameters selected.

- ***Growth of Bulk Crystals:***

To investigate the intrinsic properties of a typical material, a three-dimensional bulk crystal will be a good experimental object to start with. One of the most widely used growth methods for bulk crystals is the Bridgman method. The precursors are firstly melted in the quartz tube/crucible. By moving in a certain direction in the multizone furnace with a temperature gradient from above the melting point to below the melting point, the crystal seed in the solution can grow gradually into bulk crystal from one end of the tube to the other end. Large ingots of CsPbBr₃ bulk crystal has been successfully synthesized.²⁸ The size can reach 25 cm³, and it is crack-free and pinhole-free, as shown in figure 1.3 below.²⁹ Other methods like reversed temperature crystallization and low-temperature antisolvent-vapor saturation are also adopted for the growth of bulk all-inorganic halide perovskite crystals.³⁰⁻³¹

FIG. 1.3 a) Illustration of the Bridgman method to grow large bulk crystals. b) Picture of a crystal ingot of all-inorganic halide perovskite grown by the Bridgman method. c) High-resolution X-ray diffraction shows narrow linewidth that indicates the high crystallinity of the grown crystal. Reproduced with permission.³² Copyright 2017, John Wiley and Sons.

- **Growth of Thin Films:**

The simplest method of the thin film preparation would be one-step spin-coating by dropping prepared precursor solution on rotating substrate. Due to the low solubility of CsX in the precursor solution, the multi-step spin-coating method was developed as an alternative by separating the deposition of PbX_2 and CsX. The number of deposition cycle n of CsBr for instance determines the composition stoichiometry ($n \leq 3$: CsPb_2Br_5 , $n = 4$: CsPbBr_3 , $n \geq 5$: Cs_4PbBr_6).³³

As the solubility of the precursors matters, the morphology and composition of the thin films are influenced by the types of solvents.³⁴ Choice of solvents need to be taken into account

for optimization of the film quality. The target is to prepare smooth and uniform coverage films without pinholes and cracks.

The dual-source vacuum evaporation method helps to produce high-quality CsPbBr_3 thin films by vaporizing CsBr and PbBr_2 simultaneously towards the substrates.³⁵ The relative evaporation rate of the individual source determines the overall composition stoichiometry.

- ***Growth of Nanostructures:***

Other than three-dimensional all-inorganic halide perovskite bulk crystals and ultra-thin films, lower-dimensional structures especially nanostructures have also been synthesized and investigated. The change of dimensionality can bring novel electronic and optical properties to the material when the periodicity of the crystal lattice is broken in some directions.

CsPbX_3 nanocrystals were first synthesized by Protesescu *et al.* The quantum confinement effect of nanostructures provides leverage to modulate the optical properties of CsPbX_3 . The quantum efficiency (the number of photons emitted divided by the number of photons absorbed) can go up to 95%, and the emission linewidths can be as narrow as 12–42 nm.³⁶ By tuning the relative ratios of halide ions (Cl^- , Br^- , I^-) in the composition, the emission light of CsPbX_3 can cover a wide visible spectral range of 410–700nm. Owing to the ionic nature of halide perovskites and efficient vacancy-assisted diffusion mechanism, the anion ions of CsPbX_3 can also be easily exchanged within the lattice.³⁷ A fast halide ion exchange method at room temperature for CsPbX_3 quantum dots was illustrated by Akkerman *et al.*,³⁸ as shown in figure 1.4 (a). The structure and phase maintain the same after the fast halide ion exchange, and the optical properties of the perovskite quantum dots prepared by ion change are consistent with those prepared by direct synthesis.

FIG. 1.4 a) Schematic sketch of the fast halide exchange method. Note that the direction exchange from CsPbCl_3 to CsPbI_3 or vice versa is difficult, due to the large size difference between Cl and I anions. Reproduced with permission.³⁸ Copyright 2015, American Chemical Society. b) Controllable synthesis of all-inorganic perovskite nanostructures with different shapes and sizes. Reproduced with permission.³⁹ Copyright 2016, American Chemical Society

The thermodynamic stability of a structure is governed by the Gibbs free energy, which includes the contribution from both surface and bulk. When the size of the crystal decreases, the surface to volume ratio increases, thus the surface Gibbs free energy becomes more and more significant. For instance, α - CsPbI_3 is inclined to transform to δ yellow phase at room temperature. However, after reducing the size of perovskite, CsPbI_3 quantum dots can maintain at the black phase because of the larger contribution of surface energy.⁴⁰ For this reason, the restriction of tolerance factor can be relaxed for lower-dimension structures.

Nanostructures of CsPbX_3 can be prepared by hot injection or ligand-assisted reprecipitation (LARP),^{27, 41} as schematically illustrated in figure 5. By controlling the temperature, reaction time, type, and chain length of ligands, various shapes of nanostructures such as nanosheets (2D), nanoplatelets (2D), nanowires (1D), nanorods (1D), and quantum dots (0D) can be yielded.^{39, 42} For instance, successful fabrication of nanoplates of CsPbX_3 was achieved by Bekenstein *et al.*⁴³ The thickness of the nanoplates can be meticulously tuned with precision of monoatomic layer by the dosage of HBr in the solution.⁴⁴

FIG. 1.5 Synthesis methods of CsPbX₃ nanostructures. a) Hot injection approach. Reproduced with permission.⁴⁵ Copyright 2016, SPIE. b) ligand-assisted reprecipitation (LARP) method. Reproduced with permission.³⁶ Copyright 2016, John Wiley and Sons.

To grow perovskite structures with ideal shape, size, and quality, a deep understanding of the mechanisms and kinetics of crystal growth is required for informed and rational design of the fabrication process, along with systematic monitoring of the synthesis parameters as shown in figure 1.4 (b). Especially when it comes to large-scale commercialized film production, homogeneity and reproducibility are important to guarantee the efficiency of large-area solar cells, light-emitting diodes, photodetector, and so on.

Lead-free halide perovskites are also fabricated to replace toxic lead with non-toxic or less toxic elements. CsSnX₃ has an advantageous tolerance factor due to a slightly smaller size of Sn ion compared to Pb ion. However, Sn²⁺ is easily oxidized to Sn⁴⁺ within 5 minutes under an ambient environment.⁴⁶ Double perovskites such as Cs₂AgBiBr₆ is much more stable,⁴⁷ but there remains controversy of their optoelectronic properties, especially between theoretical predictions and experiment results. Besides, smooth and compact thin film preparation for double perovskites can be challenging.

1.1.3 Optical Properties

The most widely used material in commercialized solar cells is silicon (Si) which has an indirect bandgap. On the contrary, halide perovskite owns a direct bandgap, resulting in a higher light absorption coefficient and absorption rate. The direct bandgap can be clearly observed in the electronic structure shown in figure 1.6 (a) below. The lowest point of the conduction band and that of the valence band occurs at the same position in the first Brillouin

zone. In addition, the density of states (DOS) of all-inorganic halide perovskites can be derived from the electronic structures, as shown in figure 1.6 (b). We can see that DOS near the band edges are concentrated at the orbitals of lead and halide atoms, and thus the creation and recombination of charge carriers will mainly occur in the $[BX_6]^{4-}$ octahedrons, as indicated by figure 1.6 (c) and (d).

FIG. 1.6 a) Calculated electronic band structures of $CsPbX_3$, where Γ , R, and MI are the high-symmetry points in the first Brillouin zone. Reproduced with permission.²⁷ Copyright 2015, American Chemical Society. b) Calculated density of states of $CsPbBr_3$ contributed by different atomic orbitals. c) The electronic profiles of valence band maximum indicated by yellow highlight as well as that of d) conduction band minimum indicated of purple highlight. Reproduced with permission.³⁶ Copyright 2016, John Wiley and Sons.

As predicted and proved by theoretical calculations, all-inorganic halide perovskite $CsPbX_3$ shows very promising optoelectronic properties. Not only the photoluminescence peak position dependent on the halide ion, but also the photoluminescence decay rate is affected by the type of halide ion.²⁷ By tuning the relative ratio of halogen anion, a wide emission spectrum can be achieved. Interestingly, the photoluminescence peak position is also influenced by the

size of the perovskite nanostructures. For example, the PL peak position of CsPbBr₃ nanocubes with an edge length of 11, 7.5, and 5.5 nm appears at 514, 488, and 460 nm respectively.⁴⁸

Nanocrystals of CsPbX₃ show very sharp and bright photoluminescence. The origin of the photoluminescence (under low-density excitation) comes from exciton recombination which is a highly efficient channel for radiative charge carrier recombination. The exciton binding energy is defined as the Coulomb energy between the electron and the hole. It can be drawn parallel to the hydrogen atom model (one electron and one proton) and the exciton binding energy can be estimated as

$$E_B = Ry \cdot \frac{\mu}{m_0 \varepsilon^2} \cdot \frac{1}{n_B^2} , \quad (1.3a)$$

$$\mu = \frac{m_e m_h}{m_0 + m_h} , \quad (1.3b)$$

where Ry is the Rydberg energy (around 13.6 eV) of hydrogen atom, μ is the reduced mass, $m_0 = 9.11 \times 10^{-31}$ Kg is the free electron rest mass, m_e and m_h are the effective electron and hole mass, ε is the dielectric constant and $n_B = 1, 2, 3 \dots$ is the principal quantum number.⁴⁹ The first order exciton binding energy of CsPbCl₃, CsPbBr₃, and CsPbI₃ is calculated to be 75, 40, and 20 meV respectively.²⁷ Similarly, as an analogy to the hydrogen atom Bohr radius, the exciton Bohr radius a_B^{ex} can be evaluated as

$$a_B^{ex} = a_B^H \cdot \varepsilon \cdot \frac{m_0}{\mu} \cdot n_B . \quad (1.4)$$

The value of a_B^{ex} ($n_B = 1$) is estimated to be 5, 7, and 12 nm for X = Cl, Br, I respectively.²⁷ The larger the exciton Bohr radius, the longer the distance between electron and hole, and the smaller binding energy of the exciton. Hence, higher-order excitons ($n_B =$

2,3,4 ...) can only be observed at extremely low temperature or strong magnetic field due to the drastically decreased binding energy ($E_B \propto \frac{1}{n_B^2}$) and oscillation strength ($f[n_B] \propto \frac{1}{n_B^3}$).

When the size of the nanostructure is reduced below the exciton Bohr radius, the quantum confinement effect will take place. The motion of electrons and holes will be limited in some directions, causing a stronger overlap of their wavefunctions, and finally leading to the increment of their binding energy. For instance, the motion of the exciton is confined in the x-y plane of a 2D material when the thickness z is smaller than the intrinsic three-dimensional exciton Bohr radius. In this case, the exciton binding energy of 2D material is changed by the dimensionality:

$$2D: E_B = Ry \cdot \frac{\mu}{m_0 \varepsilon^2} \cdot \frac{1}{\left(n_B - \frac{1}{2}\right)^2}, \quad (1.5)$$

When $n_B = 1$, we can get the E_B of 2D material can be 4 times of that of 3D, which is a sizeable increase. Nevertheless, in reality, the thickness in the z-direction cannot be infinitely small. The actual exciton binding energy will depend on the relative ratio between thickness (or width if it is a quantum well) and exciton Bohr radius.

$$Quasi - 2D: E_B = Ry \cdot \frac{\mu}{m_0 \varepsilon^2} \cdot \frac{1}{\left(n_B - \frac{d_{eff} - 3}{2}\right)^2}, \quad (1.6a)$$

$$d_{eff} = 3 - \exp\left(\frac{-L_w}{2a_B^{3D}}\right), \quad (1.6b)$$

where d_{eff} is the effective dimensionality, a_B^{3D} is the exciton Bohr radius of the intrinsic 3D material, L_w is the width of the quantum well or other structures that is essentially a quantum well such as nanosheets or nanoplatelets. The effective dimensionality should be between 2 and 3 for real quantum well structures and thus the exciton binding energy is between $Ry \cdot \frac{\mu}{m_0 \varepsilon^2}$ and $4Ry \cdot \frac{\mu}{m_0 \varepsilon^2}$.

Not only the exciton binding energy change with dimensionality, but the bandgap also shifted owing to quantum confinement of wavefunctions of charge carriers. The smaller the size of the nanostructures, the stronger the quantum confinement effect, the larger the bandgap, and the shorter the wavelength of emission and absorption of light. Figure 1.7 (a) below shows the photoluminescence and absorption of CsPbBr₃ nanoplatelets.⁴⁴ 1D and 0D nanostructures shows quantum confinement effect as well in figure 1.7 (b).⁵⁰⁻⁵¹

FIG. 1.7 a) Absorption and emission peaks blue shift with reduced thickness of nanoplatelets from 5 monolayers to 3 monolayers. NPL: nanoplatelet. NC: nanocrystal. Reproduced with permission.⁴⁴ Copyright 2016, American Chemical Society. b) The optical properties change with the size and shape of the lower dimensional structures of all-inorganic halide perovskite. NW: nanowire. Reproduced with permission.⁵⁰ Copyright 2016, American Chemical Society.

1.1.4 Applications

All-inorganic lead halide perovskites can be utilized in various applications such as photodetectors, light-emitting devices, lasers, and photovoltaic devices.

Under operation conditions, solar cells must withstand the long-term light exposure, high temperature (resulting from electromagnetic wave absorption), and recurring day-night temperature cycles. Since the organic part in the hybrid halide perovskites causes thermal instability, all-inorganic halide perovskites are developed as an alternative that is more robust under heat- and light-induced stress.^{14, 52} Kulbak *et al.* demonstrated that the photovoltaic device of cesium halide perovskites and hybrid halide perovskite has a comparable performance.⁵³ The all-inorganic halide perovskite solar cells can retain their efficiency in humid air for three months while the organic ones suffer from larger than 80% loss of its efficiency within 800 hours. Furthermore, by adopting all-inorganic halide perovskite as the absorber layer as well as replacing other lapsed and costly organic layers with inorganic ones, Liang *et al.* designed an all-inorganic solar cells architecture with superior stability towards moisture and heat.⁵⁴⁻⁵⁵ These solar cells can be fabricated in an ambient environment without protection of inert gas or encapsulation and they are under high humidity and continuous acute temperature cycles from -22°C to 100°C, as shown in figure 1.8.

FIG.1.8 a) The schematic architecture of the all-inorganic perovskite solar cells. b) The energy band alignment of the solar cell. c) Power conversion efficiency (PCE) of all-inorganic perovskite solar cells and hybrid ones under 90-95% relative humidity, 25°C and d) under 100°C. e) Stable PCE of all-inorganic perovskite solar cells undergoing temperature cycles from -22°C to 100°C in humid air. Series of symbols indicate systematic measurements in the temperature cycle. Reproduced with permission.⁵⁴⁻⁵⁵ Copyright 2016, American Chemical Society.

However, many issues need to be addressed for all-inorganic halide perovskite photovoltaics to further enhance its performance. CsPbI_3 has a narrow bandgap of 1.73 eV which is suitable for sunlight capture. Nevertheless, due to the large size of I ions, the tolerance

factor of CsPbI_3 is around 0.8, and severe octahedral tilting results in lower symmetry and entropy. This leads to an inclination for CsPbI_3 to transform into the yellow phase with substantial alteration of the crystal lattice and the electronic structure. This is considered as one of the obstacles for the developing CsPbI_3 based perovskite solar cells. By adding Br anions, the tolerance factor can be slightly increased since Br atom has a smaller volume than I atom. But even a slight increase of the tolerance factor can make the mixed halide perovskite $\text{CsPbI}_{3-x}\text{Br}_x$ a more stable structure than CsPbI_3 .^{22, 56} However, the bandgap is also enlarged after adding Br ions, for example, CsPbI_2Br and CsPbIBr_2 has a bandgap of 1.92 eV and 2.05 eV respectively.⁵⁷⁻⁵⁸ The long-wavelength part of the sunlight will directly pass through the material without been absorbed since its photon energy is smaller than the bandgap of the perovskites. Therefore, the light collection efficiency and the short-circuit current J_{sc} will be limited. It is suggested that CsPbIBr_2 can be used as a front cell in tandem solar cells or semi-transparent solar cells instead. In addition, the thin film of spin-coated CsPbI_3 nanostructures is also an option if surfactant loss is inhibited.⁴⁰ To further boost the efficiency, better device design with aligned energy bands, prevention of defect formation, suppression of charge recombination at all layers and interfaces are feasible approaches towards the theoretical Shockley–Queisser efficiency.

Another potential application field for all-inorganic halide perovskites is in light-emitting devices. CsPbX_3 Quantum dot light-emitting diodes (QLED) with tunable color range was fabricated and demonstrated by Song *et al*, as illustrated in figure 1.9 (a).⁵⁹ By mixing the CsPbX_3 quantum dots of different colors, total white light emission can be achieved. Although the long-chain organic ligand can passivate the nanostructure surface and prevent agglomeration, it can also hinder the charge carrier transport in LED. One method is to wash away excess long-chain ligands attached to the surface of the nanostructures. Li *et al.* have

investigated the effect of ligand density on the CsPbBr₃ quantum dots. They found that two cycles of purifications with hexane/ethyl acetate gave the optimal results of both light emission and charge transport. Hence, a 50-fold increase of external quantum efficiency (EQE) of the device was achieved by balancing the charge injection efficiency and the surface passivation.⁶⁰ The double sword effect of surface ligand is sketched in figure 1.9 (b). Another method is to substitute long-chain organic ligands with short ones. Pan *et al.* successfully removed the oleate ligands on the quantum dots by ligand exchange method thanks to the low binding energy of the oleate ligand.⁶¹ Surface modification can further improve the device quality by making it more resistant to water. Shi *et al.* fabricated all-inorganic LED with stacks of c-Al₂O₃/n⁺-GaN/MgZnO/CsPbBr₃/PMMA/MgNiO/Au.⁶² This kind of LED demonstrates not only a robust operational stability under oxygen and moisture with no encapsulation but also a much better efficiency compared to the organic ones with hybrid halide perovskites.

FIG 1.9 All-inorganic perovskite LEDs. a) Size- and b) composition-dependent emission wavelength of all-inorganic perovskite quantum dots. c) Tunable wide spectrum covered by tailored quantum dots. d-f) QLED devices with the university logo based on the all-inorganic quantum dots can emit bright light of pure and saturated colors. g) The color coordinates of the three QLEDs in d-f) are shown in Commission Internationale de l'Eclairage (CIE) chart, forming a largely overlapped spectrum with National Television System Committee (NTSC) standard color. Reproduced with permission.⁵⁹ Copyright 2015, John Wiley and Sons. h) The effect of ligand density on the stability and carrier injection efficiency. Reproduced with permission.⁶⁰ Copyright 2016, John Wiley and Sons.

Owing to the high absorption coefficient of all-inorganic halide perovskites, they can be used to fabricate photodetectors with a large on/off ratio, short rise and decay time, and high stability, as promising alternatives to traditional silicon-based photodetector. Additionally, by using ink printing or the roll-to-roll deposition method, the all-inorganic halide perovskite layer can be facilely integrated in large-area flexible devices.⁶³ After 1000 times of bending, all-inorganic halide perovskite-based photodetectors can still maintain their photocurrent even under the ambient environment, as shown in figure 1.10 (a). In contrast, silicon has a much more rigid crystal structure, making it much more difficult to be integrated and a much higher deterioration rate for the next-generation flexible devices. Furthermore, as illustrated in figure 1.10 (c) and (d) by adding carbon nanotube (CNT) in the all-inorganic halide perovskite layer, the conductivity, responsivity, and efficiency of the flexible perovskite photodetectors can be further boosted.⁶⁴

FIG 1.10 All-inorganic halide perovskite detectors. a) Consistent photocurrent generated by CsPbBr₃ photodetectors under different bending angles. b) Stability of all-inorganic perovskite photodetectors compared to that of easily degraded hybrid ones. Reproduced with permission.⁶³ Copyright 2016, John Wiley and Sons. c) Illustration of CNT acting as fast carrier tracks. d) Band alignment and charge transfer in CsPbBr₃/CNT flexible photodetectors. Reproduced with permission.⁶⁴ Copyright 2017, American Chemical Society. e) Multicolor scintillation of all-inorganic halide perovskites under X-ray illumination. f) Demonstration of X-ray diagnostic dynamic imaging setup for living animals. g) Bright field and h) X-ray images recorded. Reproduced with permission.⁶⁵ Copyright 2018, Springer Nature.

Moreover, CsPbX₃ shows high quantum efficiency, radiation detection ability, and nonlinear properties. The large absorption cross-section of CsPbBr₃ is also very promising for nonlinear optical devices.⁶⁶ And the large atomic number of CsPbX₃ makes it a good candidate for high-energy ray detectors (figure 1.10 e-h).^{65, 67-68}

1.2 ORGANIZATION OF THIS DISSERTATION

Although all-inorganic lead halide perovskite material was successfully synthesized in the last century, its potential has only been rediscovered in 2015. Till now, the properties and the working mechanisms of this kind of material is still under the veil, urging for a comprehensive understanding. To realize commercialization of next-generation optoelectronics based on all-inorganic lead halide perovskites, the intrinsic properties, the light absorption and emission mechanisms, and the storage and operation stability need to be explored. In this dissertation, we will investigate the above aspects of all-inorganic halide lead perovskites, with the aim of more efficient and stable optoelectronic applications.

In the following chapters, we will explain the methodology of the optical spectroscopies that have been carried out all-inorganic perovskite samples in these projects. Most of the experimental setups are flexible and can be designed and rearranged for different experiment purposes. After clarifying the methodology in chapter 2, we first look into the intrinsic optical properties of all-inorganic perovskite material in chapter 3 by unveiling its dielectric constants which are the fundamentals for informed device design as well as the linkages between theoretical electronic structure calculations and experimental outcomes. Then in chapter 4, the optical absorption and emission properties are utilized to realize temperature-insensitive optical gain under two-photon pumping. The improved stability and the device chromaticity are associated with a composite structure of the all-inorganic material system. Next in chapter 5, the thermal stability and dynamics of all-inorganic perovskites are monitored to study the mechanisms of structure evolution under temperature. And finally, in chapter 6, summaries of these projects will be given, and preliminary results of the next research project plan will be presented and discussed.

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Chapter 2

Methodology of Optical Spectroscopies

In this chapter, some of the most fundamental optical spectroscopies that I have applied to investigate the optical properties of perovskites are discussed. The setup of the measurement is often customizable for different experiment purposes. Thus, it requires an understanding of the working mechanism, limitation, and capability of each component to optimize the optical system. Besides, some concerns and pitfalls are mentioned that more informed experiment design and analysis of these optical spectroscopies can be carried out.

2.1 VARIABLE ANGLE SPECTROSCOPIC ELLIPSOMETRY (VASE)

The word “ellipsometry” was first coined by Rother in the research article “The Ellipsometer, an Apparatus to Measure Thicknesses of Thin Surface Films” in 1945. The analysis ability required by ellipsometry was met by the development of computer technology in the 1970s. In 1983, Aspnes has solved the main problems lying in the spectroscopic ellipsometry measurement in the spectral range from visible to ultraviolet. And finally, in 1988, the first automated spectroscopic ellipsometer was realized by J.A.Woollam Inc.

Ellipsometry is a sensitive and non-invasive method to acquire the refractive indexes, absorption, and thickness of the material under investigation. It does not require a reference beam and it is highly accurate and reproducible even at low light levels. Ellipsometry is also suitable for in-situ measurement for monitoring the growth of thin films and change of their refractive indexes. Ultra-thin films(<10nm) can be successfully detected, characterized, and analyzed by ellipsometry. Variable angle spectroscopic ellipsometry (VASE) enables multiple measurements at various angles to further improve the sensitivity of measurement and it also enhances the accuracy of fitting simulation to experimental data.

FIG. 2.1. The a) photo and b) sketch of the set-up of VASE. c) The rotation of the sample stage and detector unit for variable angle measurement. As a result of the law of reflection and vertical angle theorem, the rotation angle of the detector unit should be twice of that of the sample stage.

The main components of VASE are the control box, the monochromator, the input unit, the detector unit, and the goniometer base. The control box monitors all the motors including the goniometer to rotate different angles for measurements. The size of the light beam is around 4 mm in diameter and can be further reduced to a smaller size by focusing probes

2.1.1 Change of Polarization upon Reflection

Ellipsometry measurements are based on the change of polarization upon reflection. The change of the polarization is dependent on the two materials on each side of the interface where the reflection occurs.

FIG. 2.2. a) Schematic graph of electric field components before and after reflection on a sample. b) Reflection coefficient of p-polarization and s-polarization light for different angles of incidence.

Light is a kind of electromagnetic wave. The electric field of the light is perpendicular to the direction of light propagation. P-polarized light is defined as light with the direction of the electric field parallel to the plane of incidence and a s-polarized light is defined as a light with the direction of the electric field perpendicular to the plane of incidence. The p-polarized light and s-polarized light forms the basis of light with any kind of polarization.

The two key parameters used in Ellipsometry Ψ and Δ are defined as below, these two parameters indicate the intensity and phase change of s- and p-polarized light upon reflection,

$$\rho = \tan(\Psi)e^{i\Delta} = \frac{\tilde{r}_p}{\tilde{r}_s}, \quad (2.1)$$

where r_p and r_s are the reflection coefficient of s- and p-polarized light respectively.

The reflection and transmission coefficient can be calculated by Fresnel's equation,

$$r_s = \left(\frac{E_{0r}}{E_{0i}} \right)_s = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t}, \quad (2.2)$$

$$r_p = \left(\frac{E_{0r}}{E_{0i}} \right)_p = \frac{n_t \cos \theta_i - n_i \cos \theta_t}{n_i \cos \theta_t + n_t \cos \theta_i}, \quad (2.3)$$

$$t_s = \left(\frac{E_{0t}}{E_{0i}} \right)_s = \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + n_t \cos \theta_t}, \quad (2.4)$$

$$t_p = \left(\frac{E_{0t}}{E_{0i}} \right)_p = \frac{2n_i \cos \theta_i}{n_i \cos \theta_t + n_t \cos \theta_i}, \quad (2.5)$$

where n_i stands for the refractive index of the light incident medium and n_t stands for that of the light transmitted medium. θ_i and θ_t are the incident and transmitted angle respectively.

With the basis of p- and s-polarized light, polarized light can be represented by a combination of these two components.

$$\vec{E} = \begin{bmatrix} \tilde{E}_p \\ \tilde{E}_s \end{bmatrix} = \begin{bmatrix} E_p e^{i\phi} \\ E_s e^{i\phi} \end{bmatrix} \quad (2.6)$$

This matrix is called the Jones vector. For example, $\vec{E} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ for p-polarized light and $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$ for s-polarized light, $\vec{E} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix}$ for left circularly polarized light and $\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix}$ for right circularly polarized light.

Now the basic mechanism of ellipsometry can be illustrated below.

FIG. 2.3. The change of polarization of light from light source to detector.

Consider a light beam passing through a polarizer that has an angle of P with respect to the plane of incidence. After transmitting through the polarizer, the light beam incident on the sample becomes a linearly polarized light $\vec{E} = \begin{bmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix}$.

Each sample has a distinct Jones matrix $\begin{bmatrix} \tilde{r}_p & 0 \\ 0 & \tilde{r}_s \end{bmatrix}$ determined by its unique optical properties. The off-diagonal elements are all zero for isotropic material. After reflection on the sample surface, $\vec{E} = \begin{bmatrix} \tilde{r}_p & 0 \\ 0 & \tilde{r}_s \end{bmatrix} \begin{bmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix}$.

The Jones matrix for analyzer is defined as $\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{bmatrix}$. A is the angle of the analyzer with respect to the plane of incidence.

Therefore, the electric field received at the detector can be expressed as a multiplication of the Jones matrix of all the elements along the optical path.

$$E_D = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{bmatrix} \begin{bmatrix} \tilde{r}_p & 0 \\ 0 & \tilde{r}_s \end{bmatrix} \begin{bmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (2.7a)$$

$$= \begin{bmatrix} \tilde{r}_p \cos P \cos A + \tilde{r}_s \sin P \sin A \\ 0 \end{bmatrix} \quad (2.7b)$$

The intensity of light equals the square of the electric field. I_D stands for the intensity of the light beam at the position of the detector.

$$I_D \propto |\tilde{r}_p|^2 \cos^2 P + |\tilde{r}_s|^2 \sin^2 P + \left[|\tilde{r}_p|^2 \cos^2 P - |\tilde{r}_s|^2 \sin^2 P \right] \cos(2A) + 2\text{Re}(\tilde{r}_p \cdot \tilde{r}_s^*) \sin P \cos P \sin(2A) \quad (2.8)$$

If we substitute equation (2.1) to simplify the equation above, I_D becomes,

$$I_D \propto 1 + \frac{\tan^2 \Psi - \tan^2 P}{\tan^2 \Psi + \tan^2 P} \cos(2A) + \frac{2 \tan \Psi \cos \Delta \tan P}{\tan^2 \Psi + \tan^2 P} \sin(2A). \quad (2.9)$$

With a rotating analyzer, A is not a constant angle but rather than a time-dependent angle $A(t)$,

$$A(t) = \omega t = 2\pi f t, \quad (2.10)$$

where f is the rotation frequency.

The final electrical signal detected is

$$V(t) = \text{DC} + a \cdot \cos(2\omega t) + b \cdot \sin(2\omega t), \quad (2.11)$$

Where DC denotes signal of direct current.

Compare with equation (2.11) and (2.9), we can find the connections between the two equations via two ratios α and β .

$$\alpha = \frac{a}{DC} = \frac{\tan^2\Psi - \tan^2P}{\tan^2\Psi + \tan^2P} \quad (2.12a)$$

$$\beta = \frac{b}{DC} = \frac{2\tan\Psi\cos\Delta\tan P}{\tan^2\Psi + \tan^2P} \quad (2.12b)$$

where α is the ratio of the cosine-wave AC to DC and β is the ratio of sine-wave AC to DC, which can be acquired when the detector transforms the light signal to an electrical signal and sent to the computer.

If we express Ψ and Δ by α and β , we can write

$$\tan\Psi = \sqrt{\frac{1+\alpha}{1-\alpha}} \cdot |\tan P|, \quad (2.13a)$$

$$\cos\Delta = \frac{\beta}{\sqrt{1-\alpha^2}} \cdot \frac{\tan P}{|\tan P|}. \quad (2.13b)$$

Thus, the two key parameters Ψ and Δ can be calculated from the electronic signal transformed by the detector. Through Fresnel's equation mentioned above, we can extract the refractive index of the medium of interest.

In the case of anisotropic material, the off-diagonal elements of the sample are not zero anymore. The Jones matrix of the sample can be written as

$$[J]_{sample} = \begin{bmatrix} \tilde{r}_{pp} & \tilde{r}_{ps} \\ \tilde{r}_{sp} & \tilde{r}_{ss} \end{bmatrix}. \quad (2.14)$$

Sequentially, the expression of α and β also need to be adjusted and Ψ and Δ need to be calculated differently from the previous method.

$$\alpha = \frac{(|\tilde{R}_{pp}|^2 - |\tilde{R}_{sp}|^2) \cos^2 P + (|\tilde{R}_{ps}|^2 - |\tilde{R}_{ss}|^2) \sin^2 P + 2[\operatorname{Re}(\tilde{R}_{pp} \cdot \tilde{R}_{ps}^*) - \operatorname{Re}(\tilde{R}_{ss} \cdot \tilde{R}_{sp}^*)] \sin P \cos P}{(|\tilde{R}_{pp}|^2 + |\tilde{R}_{sp}|^2) \cos^2 P + (|\tilde{R}_{ss}|^2 + |\tilde{R}_{ps}|^2) \sin^2 P + 2[\operatorname{Re}(\tilde{R}_{pp} \cdot \tilde{R}_{ps}^*) + \operatorname{Re}(\tilde{R}_{ss} \cdot \tilde{R}_{sp}^*)] \sin P \cos P} \quad (2.15a)$$

$$\beta = \frac{2[\operatorname{Re}(\tilde{R}_{pp} \cdot \tilde{R}_{sp}^*) \cos^2 P + \operatorname{Re}(\tilde{R}_{ss} \cdot \tilde{R}_{ps}^*)] \sin^2 P + [\operatorname{Re}(\tilde{R}_{pp} \cdot \tilde{R}_{ss}^*) + \operatorname{Re}(\tilde{R}_{sp} \cdot \tilde{R}_{ps}^*)] \sin P \cos P}{(|\tilde{R}_{pp}|^2 + |\tilde{R}_{sp}|^2) \cos^2 P + (|\tilde{R}_{ss}|^2 + |\tilde{R}_{ps}|^2) \sin^2 P + 2[\operatorname{Re}(\tilde{R}_{pp} \cdot \tilde{R}_{ps}^*) + \operatorname{Re}(\tilde{R}_{ss} \cdot \tilde{R}_{sp}^*)] \sin P \cos P} \quad (2.15b)$$

2.1.2 Thickness Measurement from Multireflection

Besides refractive indexes, ellipsometry can be utilized to estimate the thickness of thin films as well, and it is widely used in the industry for monitoring thin-film deposition and growth for high-quality devices. The thickness of the thin film will affect the interference signal and thus alter the total reflection intensity detected, as illustrated in the graph below.

FIG. 2.4. Multireflection for a sample with a single layer of thin film on a substrate.

The total reflection can be expressed as a sum of multiple reflections,

$$\begin{aligned} \tilde{E}_{total}^r = & r_{01}\tilde{E}_{incident} + t_{01}r_{12}t_{10}e^{-i2\Omega}\tilde{E}_{incident} + t_{01}r_{12}^2r_{10}t_{10}e^{-i4\Omega}\tilde{E}_{incident} + \dots \\ & + t_{01}r_{12}^{n-1}r_{10}^{n-2}t_{10}e^{-i(2n-2)\Omega}\tilde{E}_{incident} \end{aligned} \quad (2.16a)$$

$$= \left[r_{01} + t_{01}t_{10}e^{2i\Omega} \sum_2^n r_{12}^{n-1}r_{10}^{n-2}e^{-i2n\Omega} \right] \tilde{E}_{incident} \quad (2.16b)$$

where n denote the n^{th} order of reflected beam and Ω is the phase change when light travel in the thin film:

$$\Omega = 2\pi \left(\frac{d}{\lambda} \right) \tilde{n}_1 \cos \theta_1 = 2\pi \frac{d}{\lambda} \sqrt{\tilde{n}_1^2 - \tilde{n}_0^2 \sin^2 \theta_0} \quad (2.17)$$

with thickness d , wavelength λ , incident angle θ_0 and transmitted angle θ_1 . If we substitute the following identities

$$r_{01} = r_{10} , \quad (2.18a)$$

$$t_{01}t_{10} = 1 - r_{01}^2 , \quad (2.18b)$$

into equation (2.16) and convergent results can be found,

$$\tilde{E}_{total}^r = \left(\frac{r_{01} + r_{12}e^{-i2\Omega}}{1 + r_{01}r_{12}e^{-i2\Omega}} \right) \tilde{E}_{incident} . \quad (2.19)$$

We can express the pseudo-Fresnel reflection coefficient as

$$\tilde{R} = \frac{\tilde{E}_{total}^r}{\tilde{E}_{incident}} = \frac{r_{01} + r_{12}e^{-i2\Omega}}{1 + r_{01}r_{12}e^{-i2\Omega}} . \quad (2.20)$$

The ratio of the pseudo-Fresnel reflection coefficient is now used to calculate Ψ and Δ instead.

$$\rho = \tan(\Psi)e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s} . \quad (2.21)$$

2.1.3 Kramers–Kronig Relations

One thing worth noticing is that the optical constants are not independent of each other.

This is a very effective method to test whether our result is physically reasonable.

$$n(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E' k(E')}{E'^2 - E^2} dE' \quad (2.22)$$

Since refractive indexes and dielectric constants are correlated,

$$\tilde{n} = n + ik, \quad \tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2 \quad (2.23a)$$

$$\tilde{\varepsilon} = \tilde{n}^2 \quad (2.23b)$$

$$\varepsilon_1 = n^2 - k^2, \quad \varepsilon_2 = 2nk \quad (2.23c)$$

Thus, the dielectric constants also follow Kramers–Kronig relations:

$$\varepsilon_1(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E' \varepsilon_2(E')}{E'^2 - E^2} dE' \quad (2.24)$$

2.1.4 Effective Medium Approximation

Effective medium approximation (EMA) is used to calculate the effective optical constants of the composite consisting of materials with different optical constants. There are Linear interpolation EMA:

$$\tilde{\varepsilon} = f_A \tilde{\varepsilon}_A + f_B \tilde{\varepsilon}_B + f_C \tilde{\varepsilon}_C \quad (2.25)$$

where f is the volume fraction of the individual material in the composite and $0 < f_A, f_B, f_C < 1$.

There are also the Maxwell-Garnett and Bruggeman EMA that are used more generally than linear EMA to approximate the surface roughness, index grading, and so on.

$$\frac{\tilde{\epsilon} - \tilde{\epsilon}_A}{\tilde{\epsilon} + 2\tilde{\epsilon}_A} = f_B \frac{\tilde{\epsilon}_B - \tilde{\epsilon}_A}{\tilde{\epsilon}_B + 2\tilde{\epsilon}_A} + f_C \frac{\tilde{\epsilon}_C - \tilde{\epsilon}_A}{\tilde{\epsilon}_C + 2\tilde{\epsilon}_A} \quad (2.26a)$$

$$f_A \frac{\tilde{\epsilon}_A - \tilde{\epsilon}}{\tilde{\epsilon}_A + 2\tilde{\epsilon}} + f_B \frac{\tilde{\epsilon}_B - \tilde{\epsilon}}{\tilde{\epsilon}_B + 2\tilde{\epsilon}} + f_C \frac{\tilde{\epsilon}_C - \tilde{\epsilon}}{\tilde{\epsilon}_C + 2\tilde{\epsilon}} = 0 \quad (2.26b)$$

2.1.5 Mean Square Error

Unlike other spectroscopic technologies such as absorption measurement, VASE cannot provide the information of the sample directly. A model must be proposed and adjusted for fitting the measured data. The process may take several iterations as indicated by the graph below. The modeling part can be the most significant and challenging part of VASE and need to be handled with prudence.

The mean square error (MSE) is used to quantify the quality of fitting.

$$MSE = \sqrt{\frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{mod} - \psi_i^{exp}}{\sigma_{\psi,i}^{exp}} \right)^2 + \left(\frac{\Delta_i^{mod} - \Delta_i^{exp}}{\sigma_{\Delta,i}^{exp}} \right)^2 \right]} = \sqrt{\frac{1}{2N - M} \chi^2} \quad (2.27)$$

where N is the number of data points, M is the number of free parameters in the fitting, and σ represents the standard deviations, χ^2 represents the chi-square estimator as a comparison.

FIG. 2.5. The process of the VASE measurement and analysis.

2.2 TEMPERATURE DEPENDENT ABSORPTION AND REFLECTION SPECTROSCOPY

One of the most important experimental techniques in linear optical spectroscopy is absorption spectroscopy. It is usually acquired by the comparison of transmission of light with and without the sample in the optical path. From the absorption spectrum, we can identify the

optically allowed transitions and the density of states.¹ Since the spectrum features can be usually broadened or wiped out at higher temperature by electron-phonon coupling and thermal energy, absorption spectroscopy with temperature change can be useful for the observation of fine structures and evolution of spectrum features.

FIG. 2.6. The setup for temperature-dependent absorption measurement. The sample under investigation is mounted inside the cryostat.

However, sometimes limited by the opaqueness of samples or optical thickness of the deposited films, absorption spectroscopy is not possible to be performed. In this case, reflection spectroscopy serves as an alternative way to investigate the optical transitions. According to Charles Kittel,² “the optical measurements that give the fullest information on the electronic system are measurements of the reflectivity of light on single crystals.” Nevertheless, the

reflection spectrum is strongly dependent on the reflection angle and the polarization of light. It is crucial to keep these conditions the same for both sample and reference in the same series of experiments.

FIG. 2.7. The setup for temperature-dependent reflection measurement.

The setup for temperature-dependent reflection is similar to absorption. It is favorable to incorporate a lock-in amplifier in the system to improve the signal to noise ratio.³ By inserting an optical chopper, the incident light will be modulated with a preset frequency that differs from that of indoor lighting. The signal plus noise collected at the detector will be compared with the reference, and the noise of the frequencies other than the reference frequency will be rejected. In this way, the signal to noise ratio is substantially enhanced by a lock-in amplifier, which can be hard to achieve by a high-quality band-pass filter.

A cryostat is utilized for cooling down the sample. Depending on the heat insulation and He influx, the sample at the cold finger can reach 10K and below. A feedback-modulated heater near the sample stage is used to stabilize the temperature to a specific value for measurement. It is essential to keep the cryostat in a vacuum during the whole process to avoid condensation of water on the sample as well as on the wall of the chamber. Thus, it is indispensable to include a pump system as part of the low-temperature measurement unit. The optical windows enable the incoming light to be incident on the sample and the outgoing light to be collected by the detector. However, the optical window can be one of the reasons for undesired heat transfer.

A monochromator is used to disperse the light of different wavelengths to different directions. The wavelength resolution of a grating monochromator is dependent on the diffraction grating groove numbers and diffraction orders, as the formula shown below:

$$\frac{\lambda}{\Delta\lambda} = N \cdot m \quad (2.28)$$

where N stands the number of grating grooves that are illuminated, and m stands for the diffraction order. Therefore, it is an advantage to illuminate as many grooves as possible, the focal length of the last lens and the parabolic mirror (inside the monochromator) should be equal (although for demonstration purpose, the length may not be proportional in scale in figures). In practice, the entrance and exit slit width, aberrations, and the detector will also alter the wavelength resolution. With a monochromator with diffraction gratings of 6000 grooves per mm and a focal length of 0.5 m, a typical spectrum resolution can reach below 0.1 nm.

The attenuator is inserted before the sample to avoid photodegradation of the sample and to protect the detector as well. Photomultiplier tube (PMT) is a highly sensitive detector

which can multiply photogenerated electron by several electrodes to capture even small signals. However, it is often quite time-consuming when using PMT depending on the spectrum range and step since it can only record one wavelength at a time when the diffraction grating rotates to disperse that wavelength of light out of the exit slit. To record signals in a faster way for dynamic monitoring and signal mapping, a charge-coupled device (CCD) is used instead. A CCD consists of a one- or two-dimensional array of detector diodes, which can record the whole spectrum simultaneously, nevertheless as a trade-off, the wavelength range and resolution is compromised as the array size cannot be infinitely large.

It is commonly observed in papers that the absorption and reflection peaks are deconvoluted to several Gaussians. However, justifications are needed as there may exist homogeneous broadenings, localizations, etc. Moreover, Tauc plots sometimes are mistakenly used to fit the Urbach tail area caused by disorder, which leads to a shifted bandgap.

2.3 PHOTOLUMINESCENCE (PL), MICRO PL AND PHOTOLUMINESCENCE EXCITATION (PLE)

PL spectroscopy adopts lamps or more often lasers to promote the ground state electrons to an excited state. From there, the electrons and holes can go through relaxation, diffusion, trapping, detrapping, phonon interactions, etc. The electrons and holes will finally recombine radiatively or non-radiatively. Radiative recombination of electron and holes generated photons that travel and scatter in the material. Some of photons can reach the boundary of the material and finally escape the surface. These photons become emitted light. PL quantum efficiency (PLQY) η is defined as the ratio of the number of photons emitted and the number of photons absorbed. Often η is much smaller than 1, which means that the PL spectrum only represents the destiny of a minority of excited electrons, which should be kept in mind. Some

possible pathways for electrons and holes to be generated and recombine are illustrated in the figure below.

FIG. 2.8. Schematic illustrations of generation and recombination of electrons. CBM: conduction band minimum. VBM: valence band maximum. E_B : Exciton binding energy. Green arrow: absorption. Yellow arrow: radiative emission. Gray arrow: Non-radiative recombination. Narrow scribbled arrow: relaxation. Each phonon replica is separated with equal energy distance E_{pho} on the PL spectrum and their intensity decrease with the replica order number. Auger recombination involves a non-radiative recombination of an electron-hole pair near the band edges and an elevation of another electron/hole to a higher energy level by the recombination energy. Note that the pathways shown here are some of the most common ones, but they are not exhaustive. For example, emission from bounded exciton complex, exciton phonon replicas, self-traps excitons are not drawn here.

Hinted by the figure above, the signal on the PL spectrum can provide the information of bandgap, exciton recombination, phonons, energy transfer, possible defects, disorder, and impurities in the material. It is a fundamental and powerful tool to study the optical properties of materials. Time-resolved PL (TRPL) provides the information of the dynamic process of electrons after short pulse laser excitation in the time scale of femtoseconds and picoseconds, which is vital to understand the detailed behaviors of excited electrons, for example, their decay channels and lifetimes. PL spectroscopy imparts both the intrinsic and extrinsic properties of the sample, and it is an indispensable experimental technique for developing new materials of light-emitting devices and lasers.

FIG. 2.9. The a) photo and b) sketch of setup for temperature-dependent PL measurement. The long-pass filter is inserted before the entrance slot to stop stray laser light from entering the monochromator and detector. The light source is often fixed at one single wavelength (ideally), so the excitation light is indicating by a single color, different from the previous figure.

A micro-PL is a kind of PL that provides better spatial resolution and it is useful for studying microstructures. The diameter of the laser light beam should be as smaller as possible to guarantee that only sample area of interest is excited. On the left of figure 2.10, the set of lenses can narrow the laser beam size to $\left(\frac{f_1}{f_2}\right)^2$ fold smaller. For example, if f_1 is 250 mm, and f_2 is 50 mm, the size of the laser beam can be reduced to $\frac{1}{25}$ of the original size. To further minimize the laser beam size, a lens before the sample makes the collimated laser light into focused light that strikes on the area of interest. After that, the PL signal emitted by the excited sample will be collected by the microscope and transmitted into the monochromator and CCD detector by optic fiber.

FIG. 2.10. The setup for micro-PL measurement. A long-pass filter is inserted to block stray laser light. The focus area of the laser light on the sample can be tuned by the third lens. It is important to make sure that the focus point is on the sample surface not on the substrate (not easy to distinguish by eye observation).

Photoluminescence Excitation (PLE) is an analog of a reverse process of PL spectroscopy. In PL spectroscopy, the excitation wavelength is fixed, and the emission spectrum (a wavelength range) is detected. Whereas in PLE spectroscopy, the excitation wavelength is tuned for a range, while the emission is collected only for one fixed wavelength. Roughly, when the absorption of a typical excitation wavelength is stronger, more photons will be generated, and the emission should also be brighter. This indicates the PLE can reflect the absorption property of a sample, and it is used especially for ultra-thin films when the transmission/reflection signal is not pronounced.

However, the PLE spectrum is not identical to the absorption spectrum.⁴ The reason is the same as mentioned before, PL involved a more complicated process than absorption such as diffusion, relaxation, recombination, and escaping to be finally emitted out of the sample surface. For example, the absorption at one wavelength is stronger than another, but it may lead to light emission at a different wavelength from that fixed detection wavelength. Therefore, the PLE signal decrease when the absorption increased. In this sense, PLE involved more information about the behaviors of electrons. It is also an imperative method to determine the most efficient excitation wavelength to optically pump a light-emitting device of a desired color.

FIG. 2.11. The setup for temperature-dependent PLE measurement. The light source can be a lamp or a tunable laser. Depending on the monochromator resolution and laser linewidth, the detection wavelength should have some distance above the excitation wavelength range to avoid overlapping.

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Chapter 3

Temperature Dependent Intrinsic Excitonic Resonances and Complex Dielectric Constants of CsPbBr₃ Single Crystal

In this chapter, CsPbBr₃ bulk crystal was investigated by temperature-dependent reflection spectroscopy and ellipsometry. We infer the intrinsic exciton properties like the exciton transition energy, the exciton oscillator strength, exciton-polariton as well as the exciton-phonon interaction. In addition to critical optical transitions and wavelength-dependent optical constants, essential information such as absorption coefficient, absorption cross-section, optical conductivity, and dispersion relation are also acquired. This work provides significant information on the fundamental photophysics of CsPbBr₃ and would be helpful for practical applications based on inorganic perovskites.

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3.1 INTRODUCTION

Halide perovskite materials have been emerging as promising candidates for light-harvesting and light-emitting devices.¹ This kind of material possesses high quantum yield, fast mobility of both electrons and holes, long diffusion length, and facile bandgap tuning by mixing halides.² Compared to the organic-inorganic hybrid perovskites, all-inorganic lead halide perovskites have been reported to exhibit higher stabilities and competitive performances.³⁻⁵ Nonetheless, all-inorganic perovskites were much less explored than organic-inorganic hybrid ones. It is urged to clarify the fundamental photophysics of the all-inorganic perovskites to explain their favorable properties and then make better use of them. We investigated in this work the basic properties of a CsPbBr₃ perovskite single crystal by ellipsometry and temperature-dependent reflection spectroscopy. Ellipsometry and reflection spectroscopy are non-invasive and broad-spectral experiment tools to unveil the optical properties that are significant in fundamental understanding and practical applications. The spectral features identified by ellipsometry and reflectance imply the meaningful information of energy band structures of the material, which can be applied to compare with theoretical calculations and refine the vital electronic structure simulations. The wavelength-dependent optical constants are prerequisites for robust optical models that provide guidelines to design and optimize optoelectronic devices, signifying both potentials and limitations.

Herein, bulk crystals were chosen to be characterized due to several reasons. First, bulk crystals retain the intrinsic properties of the material in contrast to thin films. The properties of the latter ones often depend on the methods of the synthesis, deposition, annealing, and even the index of the solvent.⁶⁻⁸ Moreover, the stretch and compression caused by the lattice mismatch between the thin film and the substrate deforms the lattice and electronic structure of the material. Thus, sample to sample variations abound. Second, different from

nanostructures such as quantum dots, nanorods, and nanoplatelets, the intrinsic property of bulk perovskites will not be affected by the quantum confinement effect which will influence the exciton behavior, absorption spectrum, and carrier decay rate.⁹ The properties of the intrinsic perovskite bulk crystals can then be rescaled to lower-dimensional materials and be utilized as references for studies of vast morphologies of perovskites to infer the size and shape effects. Third, it was demonstrated that the photophysics of perovskites is closely linked to their grain sizes.¹⁰ Single crystals with much fewer impurities, defects, and grain boundaries, have shown superior performances over polycrystals and need to be further characterized for future applications.¹¹

In this work, the fundamental photophysics of CsPbBr₃ perovskite bulk crystal is investigated. Two discernable transitions are observed in which the higher energy one is usually absent in the photoluminescence spectrum. The different behaviors of the two transitions with respect to the temperature indicate the complexity of the electron-phonon scattering in perovskites. The dependence of the three-dimensional Wannier-Mott exciton peak positions and linewidths on temperature is analyzed by a Lorentzian model and the optical phonon energy is deduced. By measuring ellipsometry, the dielectric constants and complex refractive indices are extracted. Based on the optical constants acquired, dispersion relation, absorption coefficient, absorption cross-section, and optical conductivity spectra are presented. Finally, the oscillator strength of CsPbBr₃ is estimated to be $1.3 \times 10^{30} \text{ rad}^2/\text{sec}^2$. The large oscillator strength explains the excellent optical properties of perovskite and leads to a variety of possible applications in optoelectronic devices.

3.2 METHODS

Synthesis. The crystal was synthesized by a modified Bridgman growth method with a four-zone furnace. The thorough fabrication process can be found in ref 12. The sample studied in this work was cut from the bulk crystal. The high degree of crystallinity was demonstrated by high-resolution X-ray diffraction which showed very narrow linewidths in rocking curve measurement.¹²

Ellipsometry. Variable angle spectroscopic ellipsometry (VASE) is a non-destructive and highly sensitive instrument to study the fundamental optical properties of a material. It measures the change of polarization of light upon reflection. The perpendicular (s-) polarized light and the parallel (p-) polarized light behaves differently when reflected from the sample surface. The ratio of the reflection intensity of the s- and p- polarized light is portrayed by two parameters Ψ and Δ as $\tilde{r}_p/\tilde{r}_s = \tan(\Psi)e^{i\Delta}$. See detailed information in ref 13. The optical constants were extracted by CompleteEASE software (developed by J.A. Woollam Co.) utilizing B-spline polynomials,

$$B_i^0(x) = \begin{cases} 1, & t_i \leq x \leq t_{i+1} \\ 0 & \text{otherwise,} \end{cases} \quad (3.1a)$$

$$B_i^k(x) = \left(\frac{x - t_i}{t_{i+k} - t_i} \right) B_i^{k-1}(x) + \left(\frac{t_{i+k+1} - x}{t_{i+k+1} - t_{i+1}} \right) B_{i+1}^{k-1}(x), \quad (3.1b)$$

where k is the degree of polynomial splines, t_i is the connection point of polynomials and i is the knot index. B-spline model typically reduces the free parameters in fitting and the resulting correlations between parameters, and more significantly, it forces Kramers-Kronig consistency and ensures a physically plausible result can be obtained. The optical constants were obtained by fitting all seven spectra with each spectrum averaged by 50~150 revolutions per measurement to improve the accuracy and reliability of our results.

Temperature Dependent Reflection Spectroscopy. The reflection spectroscopy was conducted on the CsPbBr₃ perovskite bulk crystal from 10 K to room temperature in a backscattering configuration. The light source was provided by a halogen lamp, and the reflected light was collected and resolved by a monochromator and then recorded by a photomultiplier. The sample was kept in a helium-cooled cryostat with fused silica optical windows. A smooth-surface Quartz slip with no absorption peaks throughout the recorded spectrum was also measured as a reference. A chopper and a lock-in amplifier were employed to improve the signal-to-noise ratio. The reflection spectrum of unpolarized light at room temperature was also recorded by VASE in Fig. 3.2(e) as a reference to confirm the reliability of the temperature-dependent reflection setup.

Key Components of Temperature Dependent Reflection Spectroscopy:

Light source:

- i. 450W-Xenon Lamp, Horiba FL-450XOFR
- ii. Single-Lamp Housing, Horiba FL-1039/40

Lock-in amplifier: DSP Dual Phase Lock-In Amplifier, SRS (Stanford Research Systems) SR830

Optical chopper: Low Jitter Optical Chopper, SRS (Stanford Research Systems) SR540

Monochromator: Triple Grating Imaging Monochromator, Princeton Instruments SP2750

Detector:

- i. PMT (Photomultiplier Tube), Princeton Instruments P3
- ii. Integrated PMT detector housing, Princeton Instruments PD471
- iii. Detector Interface module, Princeton Instruments SpectraHub

Cryostat:

- i. Closed Cycle Cryostat, ARS (Advanced Research System) DE-204SF
- ii. Cryogenic Temperature Controller, Scientific Instruments 9700

Pump:

- i. Turbo-molecular Pumping System, Agilent Varian Mini-Task AG81

- ii. Cold Cathode Vacuum Gauge, Agilent Varian 525 K9234-311
- iii. senTorr Gauge Controller, Agilent Varian CC2C

Optical table: Vibration Isolation Optical Workstation, Kinetic Systems Vibraplane 5212-3672-31

Attributions: I have performed all the optical measurements including ellipsometry and temperature-dependent reflection spectroscopy at the school of physical and mathematical sciences, Nanyang Technological University, Singapore. I also analyzed the experimental data and wrote the manuscript. The sample was provided by Prof Song, Prof Zeng (Nanjing University of Science and Technology, Nanjing, China), and Prof Xu (School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai, China).

3.3 RESULTS AND DISCUSSION

FIG. 3.1. (a) Ψ and (b) Δ measured by VASE on the CsPbBr₃ sample. The red lines show the fitting results of multi-angle analysis for both Ψ and Δ . (c) The dielectric constants ϵ_1 (pink

dash line) and ε_2 (blue solid line) and (d) the real part of the refractive index n (pink dash line) and extinction coefficient κ (blue solid line) extracted.

We first investigated the optical transitions and dielectric functions of CsPbBr₃ perovskites by VASE. Ψ and Δ from 50 degrees to 80 degrees are shown in Fig. 3.1(a) and 3.1(b). The measurements were taken at different positions on the sample and the consistency of the experimental data indicates the homogeneity of the sample. The mean square error (MSE) of the fitting result is 3.448, which confirms the good agreement between the simulation and measurement. In Fig. 3.1(c). The imaginary part of the dielectric constant ε_2 reveals the optical transitions from the valence band to the conduction band, where an excitonic absorption peak at 2.4 eV can be clearly observed. In addition, a transition at higher energy in the UV region (ca. 3.4 eV) is also revealed, which was not observed in the photoluminescence spectrum. Note that the real part ε_1 jumps to a relatively constant value (highlighted by grey shades) after every optical transition with a general growing trend with decreasing frequency (or increasing wavelength). The reason is that every resonance from the higher energy side will contribute to the dielectric constant at the lower energy side according to

$$\varepsilon(\omega) = 1 + \sum_j \frac{f_j}{\omega_{0j}^2 - \omega^2 - i\omega\gamma_j}, \quad (3.2)$$

where ω_{0j} is the transition energy frequency, f_j is the oscillator strength and γ_j is the damping factor. This change of the dielectric constant around resonances is a typical phenomenon by the Kramers-Kronig relationship. Thus, both the real and imaginary parts of the dielectric constant confirm the existence of two optical transitions. we will discuss more about these transitions in temperature-dependent reflectance. After two optical transitions, the dielectric constant reaches a constant value of 3.73 that is close to the result of 3.8 previously calculated by density functional theory (DFT).¹⁴ In Fig. 3.1(d), the refractive index and the extinction

coefficient over the spectrum range from near-ultraviolet to near-infrared are demonstrated. Both of them are important parameters for the architecture design of optoelectronic devices.¹⁵⁻¹⁷ The lower refractive index of perovskite material (compared with CIGS, GaAs, and CdTe) for anti-reflection coating, together with the large extinction coefficient for light absorption and trapping, make perovskite ideal components in monolithic tandem solar cells to achieve higher efficiency beyond the conversion limit.¹⁸⁻¹⁹

FIG. 3.2. (a) Absorption coefficient α , (b) absorption cross-section, and (c) optical conductivity σ of CsPbBr₃ from near-ultraviolet to near-infrared. (d) Dispersion relation $\omega - k$ (blue solid line) with a linear fit (red dash line). (e) The reflection spectrum is measured by VASE.

The absorption spectrum is acquired by $4\pi\kappa/\lambda$ (where λ is the wavelength) and shown in Fig. 3.2(a), the magnitude ($\sim 10^5 \text{ cm}^{-1}$) is consistent with other perovskites.²⁰ The peak at

around 2.4 eV is the exciton absorption peak and that around 3.4 eV is the higher energy absorption peak in the UV region. The high absorption coefficient makes perovskites effective absorber layers in solar cells. Perovskite absorber layers with thickness much smaller than the carrier diffusion length would be favorable for light-harvesting, which contributes to a higher open-circuit voltage.²¹ In Fig. 3.2(b), the absorption cross-section is deduced by the following formula,

$$\tilde{n} = \frac{mN_A}{M} \quad N = \frac{\tilde{n}}{V} = \frac{\rho N_A}{M} \quad \sigma = \frac{\alpha}{N}, \quad (3.3)$$

where N_A is the Avogadro's number, m is the mass and V is the volume. The density ρ of CsPbBr₃ is ca. 4.8 Mg/m³ refers to SpringerMaterials, the molecular weight M is found to be 579.8 g/mol and thus the atomic number density N is calculated to be around 5×10^{21} /cm³. Dividing the absorption coefficient with the N , we can get the absorption cross-section spectrum. The absorption cross-section obtained here can be rescaled for nanocrystals with different sizes²² and a high absorption cross-section is essential for achieving room temperature continuous wave pumped lasers. In addition, the two-photon absorption (TPA) cross-section which is indispensable for nonlinear devices²³ is found to be proportional to the linear absorption cross-section and a reliable linear absorption cross-section is required to reduce the discrepancy of reported values of TPA.²⁴ The optical conductivity is also computed. It describes the contribution of photogenerated charge carriers to conductivity when the material is under illumination. The conductivity σ equals to the product of the angular frequency ω , the relative imaginary dielectric constant ε_2 in Fig. 3.1(c) and the permittivity in vacuum. The high optical conductivity shown in Fig. 3.2(c) implies the possible optoelectronic applications such as photodetectors and photovoltaics. Fig. 3.2(d) shows the dispersion relation $\omega - k$ of the exciton resonance. The dispersion relation is obtained by the following formula:

$$Re\{k\} = n(\omega)\omega c^{-1} \text{ and } Im\{k\} = \kappa(\omega)\omega c^{-1}, \quad (3.4)$$

where ω is the frequency and c is the speed of light in a vacuum. The linear fit of the dispersion relation gives a slope of 1.53×10^8 m/s, which is the velocity of light traveling in perovskite material. The circuitous part at the resonance frequency exhibits the typical dispersion relation of a polariton with damping. Although the photons and the excitations are often treated as independent quantities, there exists coupling between the incident electromagnetic field and the generated electromagnetic field by oscillating polarization of an optical excitation, and a polariton is created as a result of the light-matter interplay. It should be noted that the polariton here implies the coupling between excitons and free space photon modes rather than the coupling between excitons and cavity photon modes. Here we illustrate an exciton associated polariton, where the linear part of the dispersion shows the uncoupled photon propagation and the circuitous part embodies the coupling between the exciton and the visible light, which detours the original linear propagation.

In order to study the change of optical properties and three-dimensional Wannier-Mott exciton behaviors with temperature, temperature-dependent reflection spectroscopy was performed. To our knowledge, temperature-dependent reflection spectroscopy was never conducted before on CsPbBr₃ bulk crystals. The reflection spectroscopy can be used to precisely determine the transition energy positions and directly reveals the joint density of states, unlike photoluminescence spectroscopy which involves the carrier relaxation process. The reflection spectroscopy on bulk crystals is one of the most comprehensive ways to study the electronic system of a material.²⁵

FIG. 3.3. The temperature-dependent reflectance on the CsPbBr_3 bulk crystal sample (a) around the excitonic absorption region in the visible range and (b) in the UV range. The grey dots indicate the point of inflection and the red dash arrow serves as a guide to the eye. Spectra are vertically shifted for clarity.

As shown in the temperature-dependent reflectance in Fig. 3.3(a), the excitonic absorption is obvious from 10 K to room temperature. Similar line shapes were reported in other semiconductors with excitons forming at direct bandgaps.²⁶ The existence of the excitonic peak in room temperature (also from Fig. 3.1(c), Fig. 3.2(a)) indicates that the exciton binding energy is at least above the thermal energy $k_B T$ (k_B is the Boltzmann constant and T is the temperature) at room temperature, which is around 26 meV. The blue shift of the exciton

absorption peak with temperature is indicated by the inflection point and arrow in Fig. 3.3(a). This unconventional blue shift is commonly observed in lead-based material²⁷ and caused by the contribution of Pb 6s orbital to the valence band maximum of perovskites by antibonding.²⁸ We will show a detailed analysis of temperature-dependent excitonic features in Fig. 3.5. In Fig. 3.1(b), the temperature-dependent reflection at the UV region is shown. While the excitonic peak is blue shifted with temperature, the energy position of the peak at the UV region is almost invariant with temperature or even with a very slight redshift. This slight redshift is due to the joint effect of the thermal expansion of the lattice structure and the phonon-electron scattering.²⁹ The exciton in the visible range is attributed to the lowest-energy direct transition at R point in the first Brillouin zone while the peak at UV region is the second lowest energy transition attributed mainly to the M point, consistent with results from previous first principle study³⁰ of CsPbBr₃ and the optical transitions identified by ellipsometry. The different behaviors of the transitions with respect to temperature at different critical points R and M in the Brillouin zone unveil the complexity of the phonon-electron scattering in perovskites, as shown in the figure below.

FIG. 3.4. Schematic illustration of the optical transition at R and M point in Brillion zone (k space) with blue and red shift respectively in energy when temperature increases. Green arrow: absorption, creation of electron and hole pairs. Yellow arrow: photoluminescence, radiative recombination of electron and hole pairs. Blue scribble arrow: relaxation of electrons and holes to the lowest energy levels. Thick blue curve: valence bands and conduction bands. Thin dashed blue curve: exciton energy level with an energy value of E_B below the bandgap. A bandgap is composed of valence band maximum (VBM) and conduction band minimum (CBM), perovskite is a direct bandgap material since its VBM and CBM occurs at the same point in the Brillion zone.

Previous studies on hybrid perovskites also reported peaks with different shifts and attributed the phenomenon to coexisting phases or organic cations,³¹ however inorganic perovskite CsPbBr_3 have no organic cations nor phase transitions in the measurement temperature range. Thus, the redshift is not due to the monovalent cations in the cuboctahedral

cages. Moreover, this phenomenon may be intrinsic to the lead halide perovskite family, and it is not exclusive to organic-inorganic hybrid perovskites as previously assumed. A more inclusive model for the perovskite material family is needed to explain this observation, also taking into account of Rashba effect,³² spin-orbital coupling, crystal field, and all other intriguing phenomena of perovskites.

FIG. 3.5. Exciton peak positions and widths. (a) The point of inflection method to determine the peak position from derivative reflectance spectrum at 10 K. The grey dot indicates the inflection point. (b) The fit of the Lorentzian model to the reflectance spectrum at 10 K. (c) Excitonic peak positions and (d) Γ with respect to temperature. The blue dots are the experiment data and the pink solid line is the fitted curve in (b) and (d).

To extract the peak position and the linewidth of the exciton transition, we use a Lorentzian dispersion model^{11, 33-36} to describe the reflectance line shape:

$$R(\nu) = R_0 + A \times \text{Re} \left[\frac{h\nu_i - h\nu + i\Gamma}{(h\nu - h\nu_i)^2 + \Gamma^2} \exp(i\Theta) \right], \quad (3.5)$$

where R_0 is the background reflection, A is the amplitude, $h\nu_i$ is the transition energy, Γ is the broadening or damping and Θ is the phase factor. In Fig. 3.5(b), we show the fitting of the reflectance at 10 K, which gives us a transition energy of 2.367 eV, same with the result using point of inflection method³⁷⁻³⁸ by first derivative of the reflectance in Fig. 3.5(a). This validates the reliability of the Lorentzian model. Whereas the derivative spectrum gradually becomes noisy when temperature rises, the Lorentzian model is utilized from 10K to room temperature for consistency. Peak positions and peak widths at different temperatures are summarized in Fig. 3.5(c) and 3.5(d). In Fig. 3.5(d), we apply the formula $\Gamma(T) = \Gamma(0) + \gamma_{ph}T + \Gamma_{LO}/[\exp(\hbar\omega_{LO}/kT) - 1]$,³⁹⁻⁴⁰ where $\Gamma(0)$ is the broadening at 0 K, γ_{ph} is the acoustic phonon coupling strength and $\hbar\omega_{LO}$ is the optical phonon energy. The fitting results gives γ_{ph} around 35.56 $\mu\text{eV/K}$ and that the optical phonon energy around 25 meV, which is close to the results from previous studies.⁴¹⁻⁴⁴ The larger contribution of optical phonons compared with acoustic ones to the linewidth broadening is ubiquitous for polar semiconductors, which was also reported in hybrid perovskites.⁴⁵ We also observed a slight decrease of the intensity of the reflection spectrum with temperature, which suggests a slight decrease of the dielectric constant when the temperature increases. The alike phenomenon was also found in hybrid perovskites⁴⁶ and other lead composed semiconductors such as PbTe, PbSe, and PbS.⁴⁷ The dielectric constant has a direct impact on the exciton binding energy according to the hydrogen-like exciton model, $E_B = Ry \times \mu/(m_0\epsilon^2)$, where Ry is the Rydberg energy (around 13.6 eV) of hydrogen atom, μ is the effective mass and $m_0 = 9.11 \times 10^{-31}$ Kg is the free electron rest mass. The change of the exciton binding energy induced by the change of the dielectric constant could be one of the reasons why there is a lack of agreement on the exciton binding energy which governs the separation and recombination of electrons and holes in perovskites.

Finally, the longitudinal-transverse splitting observed as a stop band in the reflectance spectrum can be extrapolated to acquire the oscillator strength. A large oscillator strength is indispensable for prominent optical phenomena and for applications such as exciton-polariton lasers.⁴⁸⁻⁴⁹ Employ the formula below

$$\omega_L - \omega_T = \frac{f}{2\omega_T \varepsilon_b}, \quad (3.6)$$

where ω_T is the transverse resonance frequency equals 3.57×10^{15} rad/sec while ω_L is the longitudinal resonance equals 3.62×10^{15} rad/sec. Both parameters are deduced from the stopband structure in the reflectance spectrum at 10 K.⁵⁰ With the assumption that the damping is small at 10 K, the longitudinal-transverse splitting can be approximately estimated by the energy separation between the maximum and minimum of the reflectance line shape. Here ε_b is the background dielectric constant around the exciton resonance. From Fig. 3.1(c), we can see that the dielectric constant is different when approaching the excitonic peak from different sides of the photon energy. ε_b is around 3.69 at the high energy side, which is slightly lower than the low energy side of the dielectric constant ε_s around 3.73. The calculated oscillator strength is found to be 1.3×10^{30} rad²/sec² (~ 0.02 per formula unit), comparable with hybrid perovskites.⁵¹ According to the Lyddane–Sachs–Teller (LST) relation,⁵²

$$\frac{\omega_L^2}{\omega_T^2} = \frac{\varepsilon_s}{\varepsilon_b}. \quad (3.7)$$

We assess that $3.73/3.69$ equals 1.011, and $(\omega_L/\omega_T)^2$ equals 1.028. The accordance of the theory and the experiment result corroborates the reliability of the estimation. The large oscillator strength, high refractive index, and facile shape control of perovskite material make it a favorable candidate for an exciton-polariton laser as both a gain material and a cavity itself.

3.4 CONCLUSIONS

Inorganic halide perovskites have attracted enormous interest in recent years owing to their remarkable properties for next-generation optoelectronics. Yet their basic optical properties have been rarely explored, which failed to meet the demand of accelerating the progress of this emerging field. In this work, temperature-dependent reflection spectroscopy and ellipsometry were carried out on a CsPbBr₃ bulk perovskite single crystal. Two discernable optical transitions at around 2.4 and 3.4 eV with opposite temperature dependence were observed, indicating the complexity of the carrier-phonon scattering process in perovskites. The intrinsic transition energy, exciton-phonon interaction, exciton polariton, and strong oscillator strength ($\sim 1.3 \times 10^3 \text{ rad}^2/\text{sec}^2$) of the three-dimensional Wannier-Mott excitons were revealed. I have acquired by ellipsometry measurement the wavelength-dependent dielectric constants and the complex refractive indices which are vital for informed optical designs to achieve device performance optimization. Furthermore, the essential and elemental optical properties such as absorption coefficient, absorption cross-section, optical conductivity, and dispersion relation of CsPbBr₃ were obtained. These parameters give insights into both fundamental physics and practical applications of CsPbBr₃ perovskites. This work unveils the photophysics of inorganic perovskites as well as offers approaches to identify the optical transitions and extract essential physical parameters, which can be utilized to explore other perovskite materials and nanostructures.

APPENDIX

FIG. 3A.1 X-ray diffraction pattern of the CsPbBr₃ crystal powder. Copyright 2017, John Wiley and Sons

FIG. 3A.2 Narrow shown in high-resolution XRD. Copyright 2017, John Wiley and Sons. The linewidth of the peak is only 0.05°, indicating high crystallinity of the crystal. This value of linewidth (FWHM) is quite narrow compared to literature. [Reference: a) Liu, Y.; Sun, J.;

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Chapter 4

CsPbBr₃/Cs₄PbBr₆ Nanocomposites for Temperature-Insensitive Chromaticity Frequency-Upconverted Lasing

CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposites provide an alternative solution other than ligand-assisted surface passivation. Ligand-free CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposites showed better stability under high temperatures and intense light influx than colloidal CsPbBr₃ quantum dots. The CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposite is an advantageous candidate for non-linear frequency upconverted lasers with a temperature-insensitive stimulated emission chromaticity and sustainable emission intensity at high temperatures under repetitive laser shots.

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4.1 INTRODUCTION

In the current development of miniaturized and integrated coherent light sources, it is crucial that the stability including thermal stability can be guaranteed under operating conditions.¹⁻³ Zero-dimensional quantum dots are advantageous gain media due to their unique electronic structure and density of states (DOS) as shown in figure 1. Compared to bulk semiconductor which has a continuous DOS, the discrete DOS of zero-dimensional quantum dots is beneficial for temperature-insensitive behaviors including high characteristic temperatures.⁴⁻⁵

FIG. 4.1. The density of states (DOS) of structures with different dimensionality. When the dimensionality reduces from bulk (3D) to quantum dot (0D), DOS changes from continuous to discrete line shapes (with respect to energy). Reproduced with permission.⁶ Copyright 2016, Springer Nature.

In the class of semiconductor quantum dots, all-inorganic halide perovskites are promising candidates for next-generation optoelectronics. Especially, owing to its excellent light emission efficiency, large one-photon and multi-photon absorption cross-sections, spectrum tunability, and facile solution processing, light-emitting devices based on all-inorganic halide perovskite colloidal nanostructures has been investigated.⁷⁻¹¹ Wang *et al.* have successfully employed CsPbBr₃ nanocrystals as the active medium and achieved low-threshold and wavelength-tunable lasing.¹²⁻¹³ Moreover, frequency-upconverted stimulated emissions by two-photon and three-photon absorption were also achieved as a further step towards nonlinear optical devices.¹⁴ Frequency-upconverted lasers have demonstrated many intrinsic advantages over the one-photon counterpart and have been widely used in applications including photodynamic therapy, bioimaging, and optical data storage.¹⁵⁻¹⁸

However, there exist bottlenecks in the performance of lasers based on nanocrystals in real operations. As mentioned in Chapter 1, the passivation of the surface of the nanocrystals are crucial for maintaining their intact structures, shapes, and the quantum confinement effect. Nevertheless, during the laser operations and energy pumping, the heat generated in the device not only impedes the efficiency of the laser but also deteriorates the surface ligands of the nanocrystals.¹⁹⁻²² Temperature of the operating active region in a laser device may readily reach 100 °C, whereas the almost total loss of the surface ligand which happens before 100 °C leads to agglomeration and clustering.²³⁻²⁴ Moreover, solid-state lasers and LED devices are often fabricated in a layer-by-layer stack structure. The solution synthesized all-inorganic halide perovskites colloidal nanocrystals need to be integrated as a compact and active thin film. Photoluminescence quantum yield (PLQY) can be achieved as high as 90% for CsPbBr₃ nanocrystals in solution while PLQY for CsPbBr₃ nanocrystals in thin-film can only reach a maximum of 18%, which is also associated with labile ligands.²⁵⁻²⁶

Furthermore, chromaticity is imperative for light-emitting devices to keep color purity temperature fluctuations and excess heat.^{1,3} However, traditional semiconductor quantum dots tend to shift their emission peak wavelength under temperature variations, and thus a complex thermal management system needs to be added to keep the chromaticity.²⁷ For Instance, CdSe/CdS colloidal quantum dots not only showed redshift of the emission peak, but also rapid PL quenching at high temperature.

FIG. 4.2. a) Examples of quantum dots encapsulated in crystals including KCl, K-Na tartrate, and KBr. They are able to emit different colors under UV light. Reprinted with permission.²⁸ Copyright 2012, American Chemical Society. b) The quantum efficiency of LED based on CdSe/CdZnSeS/ZnS nanocrystal (NC) films with and without LiCl encapsulation with respect to operating hours. Reprinted with permission.²⁹ Copyright 2015, Royal Society of Chemistry.

To overcome these obstacles for semiconductor quantum dot lasers, with the inspiration from the studies in figure 4.2, we have investigated CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposites. In these nanocomposites, the CsPbBr₃ quantum dots are embedded in the Cs₄PbBr₆ host matrix. Cs₄PbBr₆ has a bandgap around 3.8 eV, much wider than CsPbBr₃.³⁰ In this work, CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposites was shown to have temperature-insensitive emission wavelengths and their performance and stability do not rely on surface ligands.

4.2 METHODS

Synthesis of CsPbBr₃/Cs₄PbBr₆ Perovskite Nanocomposites: Precursors of CsBr (0.22 g) and PbBr₂ (0.09 g) were first dissolved in a 6 ml dimethyl sulfoxide (DMSO) solution in a beaker. Then the beaker was placed into a sealed container with toluene (20 ml). The evaporated toluene vapor reacted with the precursor solution and nanocomposites slowly crystallized. After that, the nanocomposites were separated from the solvent. The synthesis process did not require high temperature. The sample is provided by Dr. Yu, Prof. Li, and Prof. Zeng (Nanjing University of Science and Technology, Nanjing, China).

Optical Spectroscopy: Because of the small size of the grown crystals, a micro-PL system was utilized to scrutinize the spontaneous and stimulated emission of a single crystal under focus. Absorption and PLE measurement were also carried out to investigate the optical transitions in the electronic structure of the material. The general setup and basic mechanisms of absorption spectroscopy, PLE, and micro PL have been discussed in Chapter 2. Temperature variations from 20 °C to 150 °C were provided by a heat stage with sensors and a built-in feedback loop.

4.3 RESULTS AND DISCUSSION

The combination of quantum dots with host matrix has already been proven to be very effective in improving the thermal stability, chemical stability, and photostability of quantum dots in previous studies such as the incorporation of quantum dots into inorganic salts (e.g. NaCl, KCl, KBr, NaNO₃).^{28, 31-32} Images of color emitting crystals containing quantum dots under UV light are presented in figure 4.2. The improved stability under environmental stressors and operational conditions is imperative for the commercialization of the all-inorganic halide perovskite nanocrystals in real applications.

In light of this, instead of ligand-assisted surface passivation, we incorporated CsPbBr₃ quantum dots in the Cs₄PbBr₆ host matrix. The schematic sketch of the nanocomposite structure is shown in figure 4.3 below.

FIG. 4.3 Schematic structure of CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposites. The green nanocube represents the dispersed CsPbBr₃ quantum dots and the blue bulk represents the Cs₄PbBr₆ host matrix.

We utilized the cost-effective and facile solution processing method for the synthesis of the fused compound. The sizes of the grown compounds are about tens to hundreds of

micrometers. The X-ray diffraction (XRD) was carried out to confirm the existence of both CsPbBr_3 and Cs_4PbBr_6 in the material, as shown in figure 4.4.

FIG. 4.4 XRD spectrum of the $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ perovskite nanocomposites. The bottom green lines come from Cs_4PbBr_6 XRD standard reference while the rhombus star indicates the signal from CsPbBr_3 .

To study the optical transitions within the nanocomposite, photoluminescence (PL) measurements were conducted with a He-Cd continuous wave laser with an intensity of 10 mW cm^{-2} at room temperature. As shown in figure 4.5 below, the composite showed different emission profiles under excitation of different wavelengths. When the sample was irradiated by laser light of 442 nm wavelength, it only showed one single strong peak around 520 nm, which comes from CsPbBr_3 .^{7, 9, 12} Whereas, if the sample is excited by the laser line of 300 nm, in addition to the green emission centered at 520 nm originated from CsPbBr_3 , a much stronger emission peak in UV region centered at 375 nm will appear, which corresponds to the emission

from the Cs_4PbBr_6 host matrix.³³⁻³⁵ Meanwhile, under 300 nm laser excitation, the amplitude of the PL peak from CsPbBr_3 dropped significantly.

FIG. 4.5 Left: PL spectrum measured on the $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ nanocomposite with an excitation wavelength of 442nm. Right: PL spectrum measured on the $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ nanocomposite with an excitation wavelength of 300 nm.

Photoluminescence excitation (PLE) measurements were also conducted for both $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ nanocomposites and CsPbBr_3 colloidal quantum dots monitored at the respective green PL peak wavelengths (520 and 512 nm for $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ nanocomposites and colloidal CsPbBr_3 colloidal quantum dots, respectively) under room temperature. In the visible range, the two spectra followed a similar trend. However, in the UV region (< 350 nm), while the PLE signal stayed strong for CsPbBr_3 quantum dots, the signal for $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ nanocomposite showed a sharp decrease, as indicated by the orange circle in figure 4.6. The reason is that the Cs_4PbBr_6 host matrix starts to absorb incoming light when the photo energy

of the excited light increases above its bandgap. This strong absorption at the bandgap of Cs_4PbBr_6 will largely deplete the light of higher photon energy (i.e. shorter wavelength) and thus only a trace of the UV laser light can enter into the encapsulated CsPbBr_3 quantum dots and then induce emission from CsPbBr_3 at a wavelength of 520 nm. The absorption and emission processes are illustrated in figure 4.7. This decrease of PLE signal at the UV region indicates that CsPbBr_3 quantum dots are embedded in the Cs_4PbBr_6 host matrix.³⁶

FIG. 4.6 PLE spectrum for the $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ nanocomposite (black line) and CsPbBr_3 quantum dots (red line). The absorption spectrum for $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ nanocomposite is also shown as the green line. The blue area indicates the spectrum range where the PLE signal of the $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ nanocomposite and CsPbBr_3 quantum dots diverge. The orange circle denotes the drop of PL signal in the UV region.

FIG. 4.7 The optical transitions in the $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ nanocomposite. If the photo energy of the excitation light is larger than the bandgap of Cs_4PbBr_6 , the excitation light will be

strongly filtered by the host matrix, leaving only weak absorption and hence emission from the embedded CsPbBr_3 quantum dots. When the photon energy of the light is smaller than the bandgap of Cs_4PbBr_6 , it will pass through the host matrix (appears transparent to the excitation light) and enter into CsPbBr_3 quantum dots. The light absorbed in quantum dots will create electrons and holes which later combine and give out the PL signal.

The ligand-free $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ perovskite nanocomposite has a great potential in real application with its improved stability. In the next step, we explored $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ perovskite nanocomposite as a potential candidate for next-generation lasers. The nanocomposite was taken under excitation of a pulsed laser with a wavelength of 800 nm. Different from the previous He-Cd continuous-wave laser, Ti-sapphire femtosecond pulsed laser provides higher energy intensity, thus nonlinear optical behavior like up-conversion can be observed. The skematic illustration of the two-photon induced stimulated emission is shown in the figure below.

FIG. 4.8 Sketch of two-photon induced frequency-upconversion stimulated emission, where $\omega_1 = c/800\text{ nm}$, $\omega_2 = c/540\text{ nm}$. Two photons of 800 nm are demanded to generate one more electron in the conduction band and one more hole in the valence band.

The sample is measured under pulse frequency of 80 MHz, pulse interval of 12.5 ns, and pulse duration of 100 fs. When the laser intensity exceeds the threshold of 2.2 mJ cm^{-2} , the CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposite shows a sharp two-photon pumped stimulated emission peak. Both the narrower line width and the transition of the slope gradient of emission intensity versus excitation intensity confirm the generation of stimulated emission.³⁷ The threshold intensity is comparable to that of colloidal CsPbBr₃ quantum dots and much less than that required for traditional metal-chalcogenide quantum dots.^{14, 38-39} To further test its thermal stability, temperature-dependent stimulated emission measurement was conducted from 20 °C to 150 °C, as shown in figure 4.9 (a). The excitation intensity is maintained at 3.5 mJ cm^{-2} , which is about 1.5-fold of the stimulated emission threshold.

Ideally, owing to the quantum confinement effect, lasers based on quantum dots have the advantage of higher PLQY and purer chromaticity.³⁷ Discrete and concentrated density of states, as shown in the appendix figure 4A.1, make quantum dots emit light with specific photon energy and thus high chromaticity. However, in device operations, the temperature fluctuations and excess heat will hinder the color purity.¹⁹ Traditional quantum dots such as CdSe will show a redshift of emission peak as the temperature increases, and thus a complex thermal management system need to be added to keep the chromaticity.¹

As shown in figure 4.9 (a) below, the two-photon frequency up-converted stimulated emission of CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposite shows temperature-insensitive

emission peak position. The decrease of the intensity of the stimulated emission peak with increasing temperature is due to thermal quenching, which is commonly observed in semiconductors, but the temperature-insensitive peak position is distinct from that of the traditional semiconductor quantum dots. The reason lies in the unique electronic structure of the perovskite system. For traditional semiconductors, when the temperature increases, the distance between the adjacent atoms in the crystal increases, thus the coupling between the atomic orbitals becomes weaker and the bandgap is shrunk. In general, the bandgap decreases quadratically as a function of the change in temperature at low temperatures, and linearly at higher temperatures for most of the semiconductors.⁴⁰ However in CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposites, the unique hybridization of atomic orbitals near the band edges makes it contrast with the traditional semiconductors.^{30, 41-43} This temperature-insensitive behavior will guarantee the chromaticity of the lasers without the implementation of a complex thermal management system. The inset of figure 4.9 (a) shows the invariance of the PLQY before and after the heating and cooling, shows the robust protection of the Cs₄PbBr₆ host matrix from thermal damage. On the contrary, the CsPbBr₃ colloidal quantum dots protected by surface ligands show not only reduced emission intensity after heating and cooling but also fast degradation under repetitive laser pulses. Both of these thermal damages of CsPbBr₃ colloidal quantum dots are irreversible. The temperature of the active region in a laser device can reach ~100 °C under operation.¹ However, previous studies have shown that the ligands of colloidal CsPbBr₃ nanocrystals are almost totally lost at 100 °C, leading to the agglomeration of nanocrystals into bulky clusters.⁴⁴ As shown in figure 4.9 (b), the stimulated emission peak of the CsPbBr₃/Cs₄PbBr₆ nanocomposite can maintain 90% of its intensity after 1.8×10^6 laser shots at 100 °C. Whereas the colloidal CsPbBr₃ quantum dots show quickly dropped and then totally diminished emission signal at 60 °C. A high thermal and photostability structure is indispensable for optical pumping by large intensity of excitation laser pulses which

is especially required for frequency up-converted nonlinear stimulated emission. Frequency up-conversion lasers are widely used in applications including photodynamic therapy, bioimaging and optical data storage.¹⁵⁻¹⁸

FIG. 4.9. a) The stimulated emission of the CsPbBr₃/Cs₄PbBr₆ nanocomposite under fixed excitation wavelength of 800nm and intensity of 1.5 P_{th} with temperature change from 20 °C to 150 °C. The inset shows the peak position and intensity are invariant after heating and

cooling. b) The stability of the SE signals under repetitive laser shots for the CsPbBr₃/Cs₄PbBr₆ nanocomposite and CsPbBr₃ colloidal quantum dots without the host matrix. SE stands for stimulated emission.

Note:

There comes controversy of the luminescence mechanisms of the green emission from Cs₄PbBr₆ in the year 2017 when our work is published, and this controversy has drawn strong interest and attention of the science community since then. In the early stage of the study of Cs₄PbBr₆, some works attributed the green emission to the exciton recombination at the direct bandgap, and claimed that this emission is an intrinsic feature of Cs₄PbBr₆.⁴⁵⁻⁴⁶ However, it is quite impossible for a material with a 150~350 meV exciton binding energy⁴⁵⁻⁴⁷ and a bandgap of 3.8 eV to give exciton emission at 2.3 eV. Moreover, pure Cs₄PbBr₆ has been successfully synthesized without any signal of green photoluminescence.^{35, 48} Thus, researchers came to the consensus that the green emission is not an intrinsic feature of pure Cs₄PbBr₆, but rather caused by impurities or defects. However, the question of whether it originates from the inclusion/impurity of CsPbBr₃ or the crystal defects of Cs₄PbBr₆, still lacks a conclusive and definite answer. There are supporting evidences on both sides. On the one hand, DFT (density functional theory) calculations show defects such as Br vacancies have a matching energy level that could be the explanation of the green emission. Besides, TEM (transmission electron microscopy) images identified only Cs₄PbBr₆ crystal structures for emissive Cs₄PbBr₆.⁴⁹ On the other hand, there are DFT calculations that show energy mismatch between V_{Br} and the emission wavelength.⁵⁰ Meanwhile, hybridization CsPbBr₃/Cs₄PbBr₆ was identified by other TEM measurements.⁵¹

FIG. 4.10. The crystal structure of a) CsPbBr₃ and b) Cs₄PbBr₆. The electronic band structure of c) CsPbBr₃ and d) Cs₄PbBr₆. Reproduced with permission.⁵² Copyright 2018, American Chemical Society. e) Theoretical calculation of density of states of CsPbBr₃ and Cs₄PbBr₆. Reproduced with permission.³⁵ Copyright 2017, American Chemical Society. f) Photos of CsPbBr₃, Cs₄PbBr₆, and CsPbBr₃ in Cs₄PbBr₆ under ambient light. Reproduced with permission.⁵¹ Copyright 2018, Royal Society of Chemistry.

To closely examine the structure-property correlation, Qin *et al.* carried out a combined confocal Raman-PL measurement with high-pressure diamond anvil cell on emissive as well as non-emissive Cs₄PbBr₆. They detected Raman signals of CsPbBr₃ from emissive Cs₄PbBr₆, and this Raman signal from CsPbBr₃ vanished when the pressure is increased to 2.0 GPa, together with the green PL signal.⁵³ It is also suggested that CsPbBr₃ can be gradually generated by phase transformation of Cs₄PbBr₆, turning the sample from non-luminescent to highly luminescent.⁵⁴ The facile and reversible phase transformation from Cs₄PbBr₆ to CsPbBr₃ is ubiquitously observed.⁵⁵⁻⁵⁶ To further study the topic, single-particle structure-property correlation measurement should be done if it is due to CsPbBr₃ inclusion; the defect nature

(V_{Br} ,⁴⁹ Br_3^- ,⁵⁷ or OH_i ,⁵⁸), formation energy, and defect concentrations should be revealed if it is due to crystal defects.

FIG. 4.11 a) Lattice matching of $CsPbBr_3$ nanocrystal in Cs_4PbBr_6 matrix. Reproduced with permission.⁵⁹ Copyright 2017, John Wiley and Sons. b) High resolution TEM showing $CsPbBr_3$ incorporated in the Cs_4PbBr_6 matrix. Reproduced with permission.⁵¹ Copyright 2018, Royal Society of Chemistry. c) Combined confocal Raman-PL measurement with high-pressure diamond anvil cell conducted on the emissive Cs_4PbBr_6 sample shows that PL disappears with $CsPbBr_3$ Raman signal at high pressure. Reproduced with permission.⁵³ Copyright 2019, American Chemical Society. d) Photos under UV light shows the transformation from non-emissive Cs_4PbBr_6 to highly-emissive $CsPbBr_3$ through $CsBr$ -Stripping. Left: In-situ monitoring of absorption spectrum during transformation. Right: In-situ monitoring of PL spectrum during transformation. Reproduced with permission.⁵⁴ Copyright 2017, American Chemical Society. Illustration of proposed possible models of defect such as e) OH_i , f) V_{Br} , and g) Br_3^- . Reproduced with permission.⁶⁰ Copyright 2020, American Chemical Society.

Since there exist evidence for both sides of the debate, Wang *et al.* proposed that there may exist three kinds of Cs₄PbBr₆ related material: non-emissive Cs₄PbBr₆, emissive Cs₄PbBr₆ caused by defects, and CsPbBr₃/Cs₄PbBr₆ hybrid.⁶⁰ The sample in this study is best explained by the last type: CsPbBr₃/Cs₄PbBr₆ hybrid. The reasons are the following: 1) XRD measurement clearly shows the signals of both CsPbBr₃ and Cs₄PbBr₆ from the hybrid material. 2) In the up-conversion stimulated experiment. The two-photon absorption of 800 nm (1.55 eV) is only able to bridge the bandgap of CsPbBr₃ (~2.4 eV), but not able to cover the bandgap of Cs₄PbBr₆ (~3.8 eV). In addition, PLE (single-photon excitation) shows that a similar intensity and trend for CsPbBr₃ and CsPbBr₃/Cs₄PbBr₆ at 400 nm, which implies a similar photoluminescence origin. In summary, the sample in this study is best explained by the last type: CsPbBr₃/Cs₄PbBr₆ hybrid with CsPbBr₃ as the emission center.

4.4 CONCLUSION

The ligand-free CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposites shows robust stability under high temperatures and intense light influx, attributing to the surface passivation and prevention of agglomeration by the host matrix. The frequency upconverted stimulated emission exhibits temperature insensitive chromaticity and it can preserve its peak intensity at high temperature under repetitive laser shots. The facile synthesis process, color purity, strong passivation, defect tolerance as well as photo and thermal stability make the CsPbBr₃/Cs₄PbBr₆ perovskite nanocomposite an advantageous candidate for non-linear frequency upconverted lasers.

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Chapter 5

In Situ Monitoring of Thermal Degradation of CsPbBr₃ Films by Ellipsometry Spectroscopy

In this chapter, the dynamic evolution of CsPbBr₃ films by in-situ ellipsometry under elevated temperatures is investigated. A fast and facile method for preparing CsPb₂Br₅ film is also proposed, thanks to the ionic nature of all-inorganic halide perovskites.

5.1 INTRODUCTION

Despite the remarkable optoelectronic properties of halide perovskites, the instability originated from the intrinsic soft and ionic nature has hindered their development towards commercialization. For instance, the efficiency of halide perovskite solar cells (25.2%) is comparable to that of single-crystal silicon ones (27.6%).¹ However, perovskite photovoltaics can only last up to one year,² which is far below the commercialisable standards of solar cell (10% efficiency over 10 years), not mentioning to compete with the silicon solar cell which can operate for more than 25 years in harsh outdoor conditions. This is one of the reasons that the stability of halide perovskites is always under heated discussion,³⁻¹⁶, and the research on this topic has risen with their rediscovery and never subsided.¹⁷⁻²⁵ Various approaches have been taken to improve the stability of halide perovskites and the incorporation of cesium element turns out to be very beneficial in stabilizing the perovskite structure.²⁶⁻³⁵ Nevertheless, there are still bottlenecks to overcome in order to take a step further in the commercialization of all-inorganic halide perovskites based applications. An urgent next step is to reveal the exact degradation mechanism of all-inorganic halide perovskites by *in situ* characterization, as suggested by Zhou *et al.* in their recent review.³⁶ In situ characterization has been applied on hybrid organic-inorganic halide perovskites to study the heat-induced degradation.³⁷ Especially, *in-situ* ellipsometry as a highly-sensitive, non-invasive tool has already been proven to be effective in the investigation of the instability of the hybrid perovskites.³⁸⁻⁴⁴

In this work, we will use *in situ* ellipsometry to study of the heat-induced degradation of all-inorganic lead halide perovskite material including as-synthesized CsPbBr₃ thin film, annealed CsPbBr₃ thin film, and CsPb₂Br₅ thin film from phase-conversion of CsPbBr₃. The work will deepen our understanding of the structural evolution of all-inorganic lead halide perovskite under thermal stressor, and also reveal the mechanism of the degradation process.

This understanding will help us in optimizing the device performance and lifetime under harsh industrial operation conditions (e.g. deep drilling). Our experiment shows that a small temperature change of c.a. 30 °C and c.a. 50 °C respectively can turn the heat exposure on CsPbBr₃ thin film from beneficial to detrimental, from reversible to irreversible, which emphasizes the importance of building a thermal profile for this kind of material for device optimization. In addition, we have shown that CsPb₂Br₅ is noticeably robust under heat and water. Although CsPb₂Br₅ is an indirect bandgap material without intrinsic emission, it can be applied in optoelectronic devices as a protection and confinement barrier/shell for CsPbBr₃ which has a direct bandgap and strong intrinsic emission. The preparation of CsPbBr₃/CsPb₂Br₅ core/shell hybrid structure can be rather facile by utilizing the phase conversion of pristine CsPbBr₃, the process can be super-fast and smooth as demonstrated in our experiment.

5.2 METHODS

PLD growth of CsPbBr₃ thin film: (Pulse laser deposition) PLD belongs to the category of physical vapor deposition (as mentioned in chapter 1). High-intensity laser pulses can ablate the source targets to form a plasma plume in the strong electromagnetic field. The word “ablate” originates from the Latin “ablātiō” which means detachment, and the action of laser ablation comprises a series of complex processes including field coupling of the photons to the target surface, particles expulsion, thermal diffusion, surface melting, network oscillations, surface resolidification, etc. Depending on the element, the plume shows various colors, similar to that of a flame test. The color of the plume generated from the perovskite source appears blue in the PLD chamber. The plume would expand and reach the substrate and the source material would condense on the substrate to grow a film. The growth process were monitored by reflection high energy electron diffraction (RHEED) with a thickness precision of monolayer.

Each peak in the RHEED signal indicates the formation of a new smooth layer. The deposition chamber was kept under ultra-high vacuum to prevent moisture and contamination.^{32, 45-48}

Temperature-dependent VASE: A heating system from 300 K to 800 K was attached to the VASE equipment. The sample was placed in the vacuum chamber with optical windows on the chamber walls that allow lamp light to pass through. A vacuum environment was maintained to protect the metal component in the equipment from oxidation. However, the pressure difference inside (nearly vacuum) and outside the chamber (atmosphere pressure) could also impose strain on the optical windows and induce birefringence in the window material, which would disrupt the polarization state of the lamplight. Thus, window effect calibrations must be carried out on a standard Si/SiO₂ wafer under vacuum conditions before any measurements. After calibration, all samples were then measured with the same angle of incidence (70 °) as in the calibration procedures.

5.3 RESULTS AND DISCUSSION

All-inorganic halide perovskite films grown by PLD on germanium substrate were chosen to be the objects under this study due to 1) films prepared by PLD can have an extremely smooth and flat surface, which is beneficial for the collection of reflection signals for ellipsometry; 2) large contrast between the reflective indexes of perovskites and germanium, making ellipsometry measurements more sensitive to the changes in perovskite films. 3) undesired backside reflections are avoided with opaque germanium substrate. The PLD grown CsPbBr₃ thin film has a cubic structure, as shown in figure 5A.2 of XRD measurement. The CsPbBr₃ thin film sample was then placed in the center of the vacuum chamber and carried out ellipsometry measurements at elevated temperatures.

FIG. 5.1. Ellipsometry on CsPbBr_3 sample at $150\text{ }^\circ\text{C}$ for 18 hours. The spectrum superpositions with each other both in a) psi Ψ and b) delta Δ graph. The definition of Ψ and Δ can be found in chapter 2.

When the sample temperature is less than or equal to $150\text{ }^\circ\text{C}$, there is no change in the optical spectra, as shown in figure 5.1 above. However, when the temperature reaches $200\text{ }^\circ\text{C}$, slow but obvious spectra change can be clearly discerned in both Ψ and Δ graphs in figure 5.2.

FIG. 5.2. Ellipsometry on CsPbBr_3 sample at $200\text{ }^\circ\text{C}$ for 48 hours. The spectra slowly change with time both in a) psi Ψ and b) delta Δ graph. Due to the large number of measurements, the legendary is omitted here and the red arrows are used instead to indicate the direction of the spectrum evolution with increasing hours.

By comparing Ψ and Δ graphs, there are consistent patterns in figure 5.2 (a) and (b) that can be observed. At the positions indicated by the red arrows, the curvatures at certain wavelengths first changed with increasing time and then slowly stabilized at later hours. These changes of curvature at certain wavelength regions in both graphs are caused by changes in optical transitions. Notice that after a wavelength of 600 nm, there is no obvious change of the line curvature due to the absence of absorption at those wavelengths (bandgap of CsPbBr₃, CsBr, and PbBr₂ are all less than 600 nm). From the left side to the right side of the spectrum, the curvature at UVB (ultraviolet B) region is attributed to CsBr,⁴⁹ and that around UVA (ultraviolet A) is attributed to PbBr₂⁵⁰ and the one at G (visible green) is caused by absorption at the band edge of CsPbBr₃. According to Kramers–Kronig relations mentioned in Chapter 2, absorption at one wavelength will cause the change of refractive index in the nearby spectrum region. Thus, we only designate the line curvature in figure 5.2 with a spectrum region instead of an exact wavelength.

As presented in figure 5.2, the line curvatures caused by optical transitions of CsBr and PbBr₂ flattened out while that from CsPbBr₃ sharpens. Although energy-dispersive X-ray spectroscopy (EDX) has shown that the CsPbBr₃ is stoichiometry balanced with a ratio of Cs:Pb:Br nearly 1:1:3 (FIG. 5A.1 in appendix), there may still exist certain areas in the thin film with a slight excess of CsBr or PbBr₂ due to the relative positions on the substrate to the source plume generated in the PLD chamber. When the temperature increases and stimulate ion migrations in the film, the excess CsBr in one area and PbBr₂ from another area can encounter and react, converting into CsPbBr₃.⁵¹ The chemical reaction formula is written as follows:

Owing to the annealing effect, CsBr and PbBr₂ were fully converted into CsPbBr₃ and the spectrum shows only dominant CsPbBr₃ signal at the end of the transformation. However, when the temperature is further increased to 227 °C (or 500K), the situation overturns. As shown in figure 5.3, signals appear again at the UVA and UVB regions. indicating that CsBr and PbBr₂ has been produced.

FIG. 5.3. Ellipsometry on CsPbBr₃ sample at 227 °C for 48 hours. The spectra slowly change with time both in a) psi Ψ and b) delta Δ graph. Due to the large number of measurements, the legendary is omitted here and the red arrows are used instead to indicate the direction of the spectrum evolution with increasing hours.

Meanwhile, the feature at the G region decreases its curvature with time. At this temperature of 227 °C, CsPbBr₃ begins to break apart and decompose to its constituent chemicals.

Finally, we increase the temperature to 250 °C, and we can see the CsPbBr₃ signal has been fading away, leading to a total degradation in figure 5.4.

FIG. 5.4. Ellipsometry on CsPbBr_3 sample at 250 °C for 30 hours. The spectra slowly change with time both in a) psi Ψ and b) delta Δ graph. Due to the large number of measurements, the legendary is omitted here and the red arrows are used instead to indicate the direction of the spectrum evolution with increasing hours.

In the meanwhile, the peak for PbBr_2 also weakened due to evaporation, whereas the signal from CsBr become the sharpest, because of its much higher evaporation temperature than PbBr_2 (as a reference, the boiling point of PbBr_2 is 916 °C under 1 atm, while the boiling point of CsBr is 1,300 °C under 1atm).

To clearly demonstrate the effect of heat exposure on CsPbBr_3 film, we cooled down the sample after each temperature assessment were finished, and then measure the sample at room temperature (RT), so that the changes of features can be compared directly. In figure 5.5, the RT ellipsometry were carried out on the sample cooled down from 150 °C, 200 °C, 227 °C, and 250 °C respectively, and the results are summarized in one graph. We can clearly see the intensification, reduction, and finally total evanescence of the CsPbBr_3 feature in the purple zone indicated in figure 5.5.

FIG. 5.5. Ellipsometry on CsPbBr_3 sample at room temperature after each temperature cycle.

a) ψ Ψ and b) δ Δ graph.

PL and EDX are employed to test the final product after heating at 250 °C. From the PL spectrum in supplementary figure 5S.1, the spectrum resembles the CsBr spectra from the previous researches.⁵²⁻⁵³ EDX in supplementary figure 5S.2 also shows Cs and Br signal and absence of that from Pb atom.

FIG. 5S.1 PL measurement of the final product after total degradation shows a similar quenching behavior and doublet emission as in previous research.⁵²⁻⁵³

FIG. 5S.2 EDX measurement of the relative ratio of elements in the CsPbBr_3 sample after the heat treatment. The difference in Cs and Br may due to the tiny amount in the final product and the decrease of the thickness of the film. The main signal comes from the underneath germanium substrate.

To confirm that the effect of annealing in the process, we put another sample under test, which has already been annealed in the PLD chamber under 500 °C with N_2 gas. Note that the effect of temperature in the PLD chamber is different from that in the ellipsometry chamber since the gas pressure is different. This condition of 500 °C with N_2 is tested to be an optimal annealing condition in the PLD chamber through HRXRD, TEM and SEM characterizations carried out by my colleagues.

We performed *in-situ* spectroscopic ellipsometry measurement on this annealed sample under the same conditions as the previous case. On the contrary of the previous sample which starts to transform at 200 °C, for this already annealed sample, the spectrum shows no change both at 150 °C and 200 °C. After that, the further evolution with temperature is similar. At

223 °C, the perovskite film begins to decompose, and it finally is left with CsBr at 250 °C, the same as the CsPbBr₃ film without annealing.

FIG. 5.6 Ellipsometry on annealed CsPbBr₃ sample with temperature of a) and b) 150 °C, c) and d) 200 °C, e) and f) 227 °C, g) and h) 250 °C. Due to the large number of measurements, the legend in e)-h) is omitted and the red arrows are used instead to indicate the direction of the spectrum evolution with increasing hours.

The absorption spectrum of the anneal CsPbBr₃ film before and after heat treatment from RT to 250 °C are compared in the following figure. The absorption peak of the final product comes from CsBr, same with the previous sample.

FIG. 5.7 the absorption spectrum of the annealed CsPbBr₃ film (a) before and (b) after heat treatment. The line shape in (a) is similar to the intrinsic CsPbBr₃ bulk crystal in chapter 3. The line shape in (b) is attributed to the absorption of CsBr.

In addition, we have also tested the thermal stability on an accidental prepared perovskite sample. In a separate experiment, one CsPbBr₃ film sample was taken out of a cold compartment (below 0 °C) directly into the air, and water condensation appears on the film surface immediately. After quickly warming it back to room temperature with a hairdryer which also rapidly dissipates water condensation, we noticed the perovskite film changes its color from yellow to pure white. We then characterized the sample under XRD and found

surprisingly sharp and narrow peaks, which indicate high crystallinity of the film. Moreover, all the signals come from CsPb₂Br₅ without any traces of CsPbBr₃.

FIG. 5.8 XRD of the perovskite sample after water condensation was removed. Sharpe peaks correspond to (002), (210), and (413) facets respectively in CsPb₂Br₅. Inset of CsPb₂Br₅ crystal structure is reprinted with permission.⁵⁴ Copyright 2017, John Wiley and Sons.

We suspect that the water also swiftly takes away CsBr since CsBr has a high solubility in water, whereas PbBr₂ remains (as a reference, the solubility in water at room temperature is 123 g/100 mL for CsBr and 0.973 g/100 mL for PbBr₂). In addition, due to the highly ionic structure of all-inorganic halide perovskites, water can infiltrate into the crystal structure expediently, solving and taking way CsBr. All the chemical reactions involved are exothermic, spontaneous and entropy favored,⁵⁵⁻⁵⁶ and the formulas are stated below:

The high crystallinity of CsPb_2Br_5 may come from the freezing temperature and short water condensation formation time. Although water is often considered undesired in the synthesis process of perovskite, in particular cases, it can be exploited to improve the material quality.⁵⁷ We measured the new CsPb_2Br_5 sample with *in-situ* ellipsometry under high temperatures in figure 5.9, and there is no significant change up to 252 °C, which shows that CsPb_2Br_5 is a more thermally stable material than CsPbBr_3 . Moreover, CsPb_2Br_5 is also more stable in humid environments since it is already an end product in the above equations associated with water transformation.

FIG. 5.9 Ellipsometry on CsPb_2Br_5 sample from 300 K (RT) to 525 K (252 °C). a) ψ Ψ and b) Δ graph. Note that in this spectrum, the temperature is not fixed, unlike the previous figures that the temperature is fixed with time variant. Each measurement is carried out at a different temperature after heating at that temperature for 6 hours. The line shape only shifts slightly due to temperature-induced change in refractive indexes both in film and substrate, ubiquitously observed in most materials. The spectrum before (red line) and after the heat treatment (purple line) coincide.

Therefore, it is very promising if we can combine the emission efficiency of CsPbBr_3 and the stability of CsPb_2Br_5 into heterostructures with better long-term performances. Furthermore, the bandgap of CsPb_2Br_5 is wider than CsPbBr_3 ,⁵⁸ which is beneficial for

confining the excitons within CsPbBr₃ to avoid surface traps when CsPb₂Br₅ is incorporated as a protective barrier.

5.4 CONCLUSION

In this work, we have utilized *in-situ* ellipsometry at various elevated temperatures to investigate the annealing effect and the degradation process of all-inorganic halide perovskites. The heat from the environment as well as device operations should be clearly controlled and monitored since even a small change from 200 to 227 °C will turn the heat influx to CsPbBr₃ material from beneficial to detrimental, and induce change from reversible to irreversible. We have also proposed a super-fast way to convert CsPbBr₃ thin film to CsPb₂Br₅ thin film with high crystalline quality. In addition, the CsPb₂Br₅ thin film is shown to be more stable under heat and water. The hybrid structure of CsPbBr₃/CsPb₂Br₅ could be beneficial for improving both stability and performance (due to dielectric confinement). The future work can include an investigation on perovskite with different mixed ratio of halogen elements. Moreover, this *in-situ* characterization method of spectroscopic ellipsometry can also be extended to the investigation of other instability issues such as polymorphic transition, hydration, oxidation caused by moisture, light, oxygen, heat, and their combinations.

APPENDIX

FIG. 5A.1 EDX measurement of the relative ratio of elements in the CsPbBr_3 sample before the heat treatment. The atomic ratio (At %) 19.00: 19.14: 61.06 is about 1:1:3 for Cs, Pb, and Br elements.

FIG. 5A.2 XRD on CsPbBr₃ sample before water condensation. The peak corresponds to (200) facet in cubic CsPbBr₃.

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Chapter 6

Conclusion and Outlooks

In this chapter, the main findings and outcomes of previous research projects is summarized and then the a future research plan is proposed with some preliminary results and discussions.

6.1 CONCLUSION

Giving the outstanding features of all-inorganic halide perovskites and their wide potential applications in next-generation light harvesting and emitting devices, it is urgent for us to take a step further on the roadmap for commercialization towards efficient and stable optoelectronics. In order to achieve this goal, it is indispensable not only to delve deeper into the fundamental mechanisms of this kind of intriguing material but also to inspect its performance beyond ideally protective conditions and circumspect settings. In this thesis, we utilized different combinations of optical spectroscopies to systematically investigate all-inorganic halide perovskites with a broad spectrum as well as a wide temperature range. We have discussed a series of aspects from the evolution of their crystal structure, to the optical transitions and oscillation strengths in the electronic structure; from theoretical device architecture design based on dielectric constants, to the thermal stability and chromaticity under device working conditions; from bulk crystals, to thin films, nanostructures and composites; from low energy probing to high energy excitation. With these works, we hope to make contributions to unleash the full potential of this enigmatic and rediscovered material.

6.2 FUTURE WORK

White light illumination is a ubiquitous necessity in daily life. Conventionally, to achieve white light emission in a single material, one or multiple dopants are needed, which are often involved with scarce and expensive rare-earth elements.¹ Besides, these rare-earth elements are also in demand in the fields of electronics, magnets, alloys, and glasses, which further limit the resource. Moreover, high temperature and high energy are required for the sintering process of rare-earth element doped compounds. Thus, it will be beneficial if white emission can be achieved from one single phosphor without doping. White light emission was

observed in layered hybrid perovskites, and the broadband emission is attributed to self-trapped excitons.²⁻³

Recently, self-trapped exciton emission of perovskite is a topic under heated discussion.¹ The concept of self-trapped exciton should be differentiated from that of defect bounded exciton. For the former one, the exciton trapping is due to the temporal deformation via phonon interactions when excitons are generated, as shown in figure 6.1. After the excitons recombine and vanish, the crystal structure will return to its initial status in a very short time. Whereas for the latter case (defect bounded exciton), the defect is localized in the crystal structure rather permanently, which can be caused during or post synthesis. Self-trapped excitons can be beneficial in applications such as solar concentrators (because of large Stokes shift), multi-photon bioimaging (due to long emission lifetime), and white light-emitting diode as mentioned earlier.

FIG. 6.1 Illustration of the mechanisms of self-trapped exciton formation and recombination. a) Energy diagram of the temporarily formatted self-trapped excitons (STE). b) The broadband emission and large Stokes shift are caused by phonon interactions. Reproduced with permission.¹ Copyright 2019, American Chemical Society.

The formation mechanism of self-trapped excitons suggests that they prefer to occur in soft structures with small deformation energy. As mentioned in chapter 1, the halide perovskite has an ionic and soft structure. In addition, the deformation energy decreases with the crystal dimensionality. Till now, self-trapped excitons have been observed in zero-dimensional,⁴⁻⁵ one-dimensional,⁶ two-dimensional perovskite structures,^{2, 7} and double perovskites.⁸⁻⁹ It inspires us to investigate whether self-trapped excitons also exist in three-dimensional all-inorganic halide perovskite structures.

Here we discovered broadband emission from CsPbBr₃ by temperature-dependent photoluminescence. Interestingly, the emission line shape depends both on the temperature and the excitation wavelength (442 nm and 325 nm).

FIG. 6.2 Temperature-dependent photoluminescence under 442 nm excitation from 10K to 300K.

FIG. 6.3 Temperature-dependent photoluminescence under 325 nm excitation from 10K to 300K.

Notice that this phenomenon is different from what we have discussed in chapter 4 of the $\text{Cs}_4\text{PbBr}_6/\text{CsPbBr}_3$ perovskite nanocomposite under two excitation wavelengths. The broad emission in figure 6.3 cannot come from Cs_4PbBr_6 . The reason is that 1) the emission profile is different. 2) no signal of Cs_4PbBr_6 in XRD measurement. The emission peak is also never reported in CsBr and PbBr_2 , which rules out the possible origins of excess precursors. The optical transition is excited by UV light while the emission peak is around 600-700 nm. This indicates a large Stokes shift, which is one of the features of self-trapped excitons.

The intensity of broadband emission first increases with the temperature, then it starts to decrease. The trend can be the result of competition between thermal activated phonon interactions and the tendency to form a more symmetric cubic crystal structure (less distortion) when temperature increases.

To further test if the origin of the broadband emission comes from the self-trapped excitons, we have conducted excitation intensity-dependent photoluminescence measurement.

FIG. 6.4 Integrated PL intensity versus excitation intensity in log-log scale.

The integrated emission intensity shows a linear relationship with excitation intensity in figure 6.4, which indicates that the broadband emission does not come from permanent defects in the crystal structure.²

In our future plan, transient absorption spectroscopy can be conducted to give further evidences. According to the mechanisms illustrated in figure 6.1 (b), the self-trapped time is related to the vibration time of phonons (around several hundred femtoseconds). If the transient

absorption spectroscopy has a sufficiently high time resolution, it may be possible to directly observe the optical transitions associated with the temporal STE states.

FIG. 6.5 Temperature-dependent photoluminescence of CsPbBr₃ film on STO under 325 nm excitation from 10K to 300K.

Interestingly, perovskite films grown in the same condition but with a different substrate of SrTiO₃ (STO), the photoluminescent signal under 325 nm excitation only shows the intrinsic sharp peak, as shown in figure 6.5. The choice of the substrate and lattice mismatch can influence the crystal structure and the morphology of the film. Smith *et al.* have claimed that the origin of the broad emission in perovskites comes from the distortion of the bond between the octahedrons.⁷ The PL signal comes mostly from the perovskite surface, where the periodicity of the crystal structure is terminated and the relative positions of the lead bromide octahedrons are less restrained. We think this can be one of the reasons and further experiments and calculations are to be done to confirm this hypothesis.

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