Structural evolution and optical properties of hybrid lead halide perovskites under high pressure and low temperature

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

STRUCTURAL EVOLUTION and OPTICAL PROPERTIES of HYBRID LEAD
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TINGTING YIN

**CENTRE for DISRUPTIVE PHOTONIC TECHNOLOGIES
SCHOOL of PHYSICAL and MATHEMATICAL SCIENCES**

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TINGTING YIN

Centre for Disruptive Photonic Technologies

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Publications and conference contributions

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Abstract

Hybrid lead halide perovskites with chemical formula of APbX_3 for 3-dimensional (3D) structures, and A_2PbX_4 for 2-dimensional (2D) structures, where $\text{A} = [\text{CH}_3\text{NH}_3 \text{ (MA)}, \text{NH}_2\text{CH}_2=\text{NH}_2 \text{ (FA)}, \text{C}_4\text{H}_9\text{NH}_3 \text{ (BA)}]$, $\text{X} = [\text{Cl}, \text{Br}, \text{I}]$, comprise a set of fully corner-sharing inorganic PbX_6 octahedra and organic cations at the center for 3D perovskites and corner-sharing sheets of inorganic Pb-X octahedra partitioned by organic cations for 2D perovskites. These materials endow remarkable electronic and photovoltaic properties, exhibiting huge potential application in lasers, light-emitting diodes (LEDs), and solar cells. Exploration to such materials is still at early stage and full assessment of their structures and properties will no doubt further strengthen their understanding and potential applications. High pressure and variable temperature are clean and convenient tools for such investigation as they allow easy access to various structures and interactions among the constituent atoms and molecules.

In this thesis, we study the pressure and temperature effects on the structure distortion in the hybrid perovskite family, to address the inorganic PbX_6 octahedra tilting and organic cations disorder-ordering, which significantly modify the physical and chemical properties. Chapter 4 deals with the temperature effect on the hydrogen-bonding in 3D MAPbBr_3 hybrid perovskite. We demonstrate that the H-bonds in the NH_3 end of the MA group shows sequential changes while the H-bonds in the CH_3 end only form H-bonding with the Br ions in the orthorhombic phase. High-pressure effect on the MAPbBr_3 nanocrystals (NCs) is studied in Chapter 5, where high pressure-induced comminution of NCs and sintering into large thin nanoplates (NPs) are observed for the first time. We present a detailed theoretical simulation to show that the splitting of the NCs is along a crystal plane that involves no breaking of the chemical bonds of the inorganic atoms. In Chapter 6, we report for the first time a systematically high-pressure study of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ (BAPI) 2D layered perovskite with $n=1$, where structural transitions cross all pressures are resolved and the structure-property correlation is established.

Chapter 1 Introduction to Perovskites and Motivation

Hybrid organic-inorganic perovskites (HOIPs) are low-cost and highly efficient optoelectronic and photovoltaic materials for applications in solar cell¹⁹, light emitting diode (LED)²⁰, photodetectors²¹ and lasers²², arising from their long carrier diffusion lengths^{23, 24}, and tunable spectral absorption rang^{25, 26}. These excellent properties of hybrid lead halide perovskites correlated with their fundamental and intrinsic crystal structures, which associated with the various tilting of the inorganic lattice and the order-disorder behaviors of the organic cations²⁷⁻²⁹. Thus, it is important to study the interaction between the inorganic lattice and the organic cations, *i.e.*, the hydrogen-bonding between the inorganic anions and H atoms of organic cations, to comprehensively understand the chemical and structural stabilities in HOIPs. Since Raman spectroscopy is a unique tool for characterizing the temperature-dependent vibrations of light atoms, such as H, C and N, studying the Raman spectra can resolve the hydrogen-bonding states of the HOIPs during the polymorphic transformations. On the other hand, it is important to understand the relationship between the crystal structures and the functional properties of the HOIPs to develop new crystal structural phases and physical properties toward stable and long-term photovoltaic applications in future clean energy generation and optoelectronic applications in light-emitting devices. High pressure (up to gigapascal), is able to probe the structure-property correlation of solid materials at the atomic level, where both crystal structures and electronic properties change dramatically beyond chemical modification methods.

This chapter will discuss these important issues with recently published experimental and theoretical works. Firstly, the hybrid perovskite crystal structure, related structural distortion and electronic structures will be introduced to explore

the effects of temperature and pressure on perovskite materials and then address the importance of hydrogen bonding on structural stability and functional properties. The following discussion will be focused on the dimensionality to point out the difference between 3D, 2D and nanocrystals of hybrid perovskites to address the reason for sample selection in my thesis.

1.1 Crystal structure

The general formula of intrinsic perovskites is AMX_3 , where A and M are cations and X is an anion, as shown in Fig. 1.1 (a). One M cation is coordinated to 6 X anions, while one A cation is coordinated to 12 X anions, leading to a typical cubic structure³⁰. By replacing A with organic cations ($CH_3NH_3^+$, MA; $HC(NH_2)_2^+$, FA), M with Pb cation and X with halide anions (Cl, Br, I), the first hybrid organic-inorganic lead halide perovskites were synthesized in 1978³¹, as shown in Fig. 1.1 (b). Hybrid lead halide perovskites contain an anionic lead-halogen semiconducting framework, *i.e.*, inorganic cage, and charge-compensating ammonium salts, *i.e.*, organic molecule.

The tolerance factor,

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

where R_A is the radius of the A-cation; R_B is the radius of B-cation and R_X is the radius of the halogen anion of those hybrid organic-inorganic halide perovskites. The calculated t of a series of halide perovskites are between 0.9~1 (Fig. 1.1 (c)), demonstrating the high-symmetry cubic nature of hybrid halide perovskite crystal structures in ambient condition¹.

Fig. 1.1 (a)-(b) Crystal structure of a classical perovskite and hybrid lead halide perovskite. (c) Tolerance factor (t) of a series of halide perovskites¹.

1.2 Structure distortions

The intrinsic perovskites with the typical cubic structure, where MX₆ octahedra are corner-shared with each other and A cations reside in the building block of octahedra, undergo a series of structural phase transformations via the octahedron tilts and the cation displacements. Octahedral tilts have a far greater effect on lattice parameters and unit-cell symmetries, triggering the structural deformation from one phase to another one^{2, 32}. When an octahedron is tilted in some direction it causes the neighboring octahedra tilting in the opposite ways, resulting 23 possibilities for the final structure and classified into 4 groups², as demonstrated by stereophotographs in Fig. 1.2. For example, the Glazer notation of $a^0b^+c^+$ describes no tilts about x axis, same rotation direction but different rotation angles about y and z axes for two neighboring octahedra. However, the order-disorder behaviors of the MA cations should also be involved for the structural transitions, because the A cations

with a certain symmetry in either a random or an ordered fashion will definitely induce structural deviations from the ideal structures. Dielectric relaxation and calorimetry measurements demonstrated the fully disordered MA cations in the cubic structure^{33, 34}, where the MA cation (with C_{3v} molecular symmetry) is disordered over 12 $\langle 110 \rangle$ directions to satisfy O_h symmetry and $PbBr_6$ octahedral topology creates a regular cubic network³⁵. Nuclear magnetic resonance spectroscopy (NMR) studies suggested that MA are partially disordered with eight-fold disorder in the tetragonal phase^{36, 37}. While the MA cations are fully ordered with head-to-tail fashion in the orthorhombic structure³⁸⁻⁴⁰.

Fig. 1.2 Stereo-photographs of the eight representative octahedra in each tilting arrangement, where a, b, c letter represents the rotation magnitude, +, -, 0 superscript represents the same rotation direction, opposite rotation direction, and no rotations.²

As reported, high pressure^{3, 41-45}/low temperature⁴⁶⁻⁵⁰ induced $MAPbX_3$ family ($X=Cl, Br, I$) phase transitions, the typical structural evolution of $MAPbBr_3$ perovskite upon cooling and under compression as shown in Fig. 1.3. At ambient condition, there is no tilts ($a^0a^0a^0$) of $PbBr_6$ octahedra in cubic $Pm\bar{3}m$ phase⁵¹ and MA cations are randomly disordered⁵². For example, upon cooling, $PbBr_6$ octahedra obey $a^0a^0c^-$ two tilting configuration, leading to the tetragonal $I4/mcm$ structure^{51, 53} with the partially ordered MA cations.^{54, 55} Finally, $MAPbBr_3$ perovskite transforms

into orthorhombic $Pnma$ structure via $a^-b^+a^-$ three tilts of $PbBr_6$ octahedra^{51, 53} and the MA cations become totally ordered with head-to-tail configuration⁴⁰.

In a word, the structural phase transformation in organic-inorganic hybrid perovskite is corrected with the octahedral tilting and organic cation rotating, indicating a strong interaction between X anions and H atoms of A cation. It is important to address this interaction, *i.e.*, hydrogen-bonding, to further understand the structural stability of the organic-inorganic hybrid perovskites, which will be mainly discussed in Chapter 4.

Fig. 1.3 Structure evolution of MAPbBr₃ perovskite with decreasing temperature (top panel) and with increasing pressure³.

1.3 Electronic structures

Hybrid perovskites demonstrate electronic features of conventional inorganic semiconductors, where the valence band and conduction band are determined by the

atomic orbitals of the X anions and M cations⁵⁶. In the hybrid lead halide perovskites, the electronic configuration of Pb is $6s^2 6p^0$ and the halide X is np^6 . The valence band maximum (VBM) is formed from the Pb 6s-X np σ anti-bonding combination, while the conduction band minimum (CBM) is formed from the Pb 6p-X ns σ and Pb 6p-X np π anti-bonding orbitals^{5, 39} but mostly shows a nonbonding Pb 6p character^{57, 58}, as demonstrated by the isosurface plot⁴ of Fig. 1.4 (a) and molecular orbital diagram⁵ of Fig. 1.4 (b) for MAPbI₃ perovskite. By moving I to Br to Cl, the atomic orbitals change from 5p to 4p to 3p, the valence band will be down shifted obviously while the conduction band will be up shifted a bit⁶, the calculated band structures for different halides as shown in Fig. 1.4 (c-e). For this reason, mixed-halide perovskites, such as MAPbI_{3-x}Cl_x or MAPbI_{3-x}Br_x or MAPbBr_{3-x}Cl_x are good candidate for tunable light-emitting diodes^{7, 59, 60} and lasing^{61, 62}. Note that from section 1.2, high pressure/temperature will drive perovskites structural distortion with various angles and lengths of Pb-X-Pb bonds, definitely changing their corresponding optical properties. The pressure-induced band-gap narrowing of MAPbI₃ perovskite in *I4/mcm* phase and a blue jump from *I4/mcm* to *Imm2* phase transition was reported by L.P. Kong *et al.* (Fig. 1.5 (a)), they demonstrated that the bond-length shrinkage in *I4/mcm* structure will enhance the coupling of the Pb *s* and I *p* orbitals and push the VBM up, resulting in the red shift in band gap

Fig. 1.4 (a) Isosurface plot of the self-consistent electron density of MAPbI₃⁴. (b) Molecular orbital diagram for the interaction between Pb and I atoms⁵. * represents an antibonding orbital. (c-e) Calculated band gap for MAPbX₃ (X=I, Br, Cl) at the SOC-GW level⁶.

in low-pressure range. On the other hand, the smaller angle of Pb-I-Pb bond in the *Imm2* structure makes Pb-I-Pb bond partially broken and weakens the coupling of the Pb *s* and I *p* orbitals, resulting in the blue jump (Fig. 1.5 (b))^{7, 43}. M.I. Dar *et al.* reported the unusual red shift and dual emission in MAPbI₃ perovskite upon cooling (Fig. 1.5 (c))⁸. they demonstrated that the shrinkage of lattice drives the red shift with decreasing temperature⁶³ and the two PL peaks (< 120K) are associated with the organic molecular disorder in orthorhombic domains (Fig. 1.5 (d))⁸.

In a word, the electronic band structure of hybrid lead halide perovskites is mainly determined by the coupling of Pb 6s²6p⁰ and the halide X np⁶ orbitals, while the organic cations indeed play a role in optical properties due to hydrogen-bonding interactions^{33,41,29}.

Fig. 1.5 (a-b) Pressure-induced band-gap evolution of MAPbI₃ and schematic models of the pressure-induced red shift and blue jump⁷. (c-d) Temperature-dependent PL evolution of MAPbI₃ and calculated E_g evolution as a function of lattice parameter upon cooling⁸.

1.4 Dimensionality

1.4.1 Bulk to low-dimension perovskites and nanostructured perovskites

The size of organic cations discussed in section 1.1 should be small enough to fit into the PbX₃ inorganic building blocks of the 3D framework. Otherwise, larger organic cations will break the parent 3D (AMX₃) perovskite structures into lower-dimensional perovskites, *i.e.*, 2D structures (A₂MX₄), 1D (AMX₅) or 0D (A₂MX₆), possessing the same unit structure (the top of Fig. 1.6)^{30, 64}. In the 3D perovskites, one PbX₆ octahedron is corner-sharing with 6 neighbors and organic cations reside in PbX₃ inorganic cages^{64, 65}. In the 2D perovskites, one PbX₆ octahedron is connected with 4 neighbors in layered sheets and each PbX₄ inorganic layer is

sandwiched between organic cations layers^{64, 65}. In the 1D perovskites, one PbX_6 octahedron is connected with 2 opposite neighbors in a chain and totally isolated PbX_6 octahedra in 0D perovskites^{64, 65}. With decreasing the dimensionality, the corresponding binding energy and band gap will increase due to strong quantum confinement effect^{66, 67}. In principle, nanostructured perovskites can be synthesized with all kind of inorganic frameworks from 3D to 0D, such as plate, wire, sphere, cube, etc. shape, as shown in the bottom of Fig. 1.6. The physical properties of perovskite nanocrystals are various from the bulk counterparts and are mainly determined by their size and shape⁶⁸⁻⁷⁰.

Fig.1.6 Schematic of perovskite frameworks (3D to 0D) evolved from PbX_6 inorganic octahedra (top)⁴⁵ and nanocrystals with different degree of confinement (bottom)⁹.

1.4.2 2D layered perovskite and excitonic structures

Compared to 3D hybrid perovskites, two-dimension (2D) layered hybrid perovskites, the quantum well structures⁷¹ (the inorganic layer is semiconductor with small bandgap and the organic layer is insulator with large bandgap as shown in Fig. 1.7 (b)), where electrons and holes are strongly confined within the inorganic layers to form excitons at room temperature with binding energies of $\sim 300\text{-}400\text{ meV}$, exhibit remarkable excitonic structures^{5, 15, 72}, high photoluminescence yield^{73, 74} and white-light emission properties⁷⁵⁻⁷⁷. Such quantum well thickness can be adjusted from infinite to multiple to monolayer, such as butylammonium lead iodide $((\text{C}_4\text{H}_9\text{NH}_3)_2 (\text{CH}_3\text{NH}_3)_{n-1} \text{Pb}_n \text{I}_{3n+1})$ in Fig 1.7 (a)¹⁰. In one extreme case ($n=1$), the perovskite structure becomes a perfect quantum well with only one atomic layer of PbI_4^{2-} sandwiched by organic chains, *i.e.*, $(\text{C}_4\text{H}_9\text{NH}_3)_2 \text{PbI}_4$ (BAPF), which will be discussed in Chapter 6. In the opposite case ($n=\infty$), the perovskite structure becomes a 3D cubic structure. By varying the value of n between 1 and ∞ , the 2D layered perovskites possessing multiple quantum well structure are obtained and the related optoelectronic properties of the quantum well can be tuned (Fig. 1.7 (b))^{73, 78}. The electronic structure of 2D perovskites is quite distinct from 3D perovskites, the bonding diagram of the 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 2D $(\text{C}_4\text{H}_9\text{NH}_3)_2 \text{PbI}_4$ as shown in Fig. 1.7 (c). Based on section 1.3, the VBM for the 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ originates from the Pb 6s–I 5p σ anti-bonding orbital, and the CBM is formed by the Pb 6p – I 5s σ anti-bonding and Pb 6p – I 5p π anti-bonding orbitals^{5, 39}. In the 2D $(\text{C}_4\text{H}_9\text{NH}_3)_2 \text{PbI}_4$, the electronic orbitals of the in-plane and out-of-plane I atoms of I1 and I2 (inset of Fig. 1.7 (c)) are split in a two-dimensional ligand field. The VBM consists of the Pb 6s–I1 and I2 5p σ anti-bonding orbitals, while the CBM of Pb 6p–I1 5s σ anti-bonding and Pb 6p –I1 5p π anti-bonding orbitals exhibits greater dispersion than the Pb

6p–I2 5s σ anti-bonding band⁵. It is shown that the bandwidth is narrowing and the gap is widening from 3D to 2D perovskites, leading to a high exciton stability in 2D perovskites.

Fig. 1.7 (a) Schematic crystal structures of the 2D layered perovskite, $(C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ ¹⁰. (b) Concept of quantum well in 2D layered perovskites. (c) Electronic structure evolution from original isolated PbX_6 octahedron to 3D hybrid lead perovskites to 2D hybrid lead perovskites⁵. The inset of the part of crystal structure of 2D $(C_4H_9NH_3)_2PbI_4$.

1.5 Organization of this dissertation

The main aim of this PhD thesis is to explore the pressure and temperature effects on the structure distortion in the hybrid perovskite family, to address the relationship between the inorganic PbX_6 octahedra tilting and organic cations disorder-ordering, which significantly modify the physical and chemical properties, including structural stability and morphology changes, light emission properties and carrier dynamics.

There are seven chapters in this dissertation.

Chapter 1 is the background about the organic-inorganic perovskites, including crystal structural, electronic properties and dimensionality. Related examples are listed for high pressure and temperature-dependence studies in this kind of materials. The research motivation and target are also introduced.

In Chapter 2, the main techniques and optical setups are introduced, including high-pressure technique, low-temperature apparatus and Raman and photoluminescence (PL) spectroscopy. Besides, the assistant experiments performed by my collaborators, including powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and first principle calculations, are also briefly introduced.

Chapter 3 will describe the sample synthesis processes, including the MAPbBr₃ perovskite single crystals and nanocrystals, BAPI 2D layered perovskite single crystals.

Chapter 4 focuses on the study of the hydrogen-bonding states between the H atoms of the MA cation and the halide ions by combining *ab initio* calculations with temperature-dependent Raman scattering and XRD measurements on MAPbBr₃ hybrid perovskites. Upon cooling, the H-bonding in the NH₃ end of the MA group shows sequential changes while the H atoms in the CH₃ end only form H bonds with the Br ions in the orthorhombic phase, leading to a reduction in the rotational freedom of MA and a narrowing for MA Raman modes. The hydrogen-bonding drives the evolution of temperature-dependent rotations of MA cation and the concomitant tilting of PbX₆ octahedra with the consequent dynamical change of the electronic band structures, from indirect bandgap to direct bandgap along with PL emission enhancement of ~ 60 times upon cooling. We experimentally and

theoretically reveal the evolution of hydrogen-bonding during polymorphic transformations, the different types of hydrogen-bonding lead to specific optoelectronic properties and device applications of hybrid perovskites.

Chapter 5 presents for the first time the high pressure-induced comminution and recrystallization of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs into uniform single-crystalline NPs. Instead of pressure-driven direct assembly in previous metallic/inorganic semiconductor nanoparticles, the pressure-induced comminution in the organic-inorganic hybrid lead perovskites correlates to the structural nature of PbBr_6 octahedra tilting and MA cations ordering under compression. Compared to the initial perovskite NCs, the pressure-resulting NPs exhibit a ~15 times PL enhancement and a half-short carrier lifetime. Our results provide new insights into the microscopic growth mechanisms of organic-inorganic hybrid perovskite nanomaterials under high pressure, and demonstrate a new method for engineering their morphology and associated optoelectronic properties.

In Chapter 6, a clear relationship between the crystal structure and excitonic property in 2D layered hybrid perovskite is established via a comprehensive pressure study on BAPI perovskite single crystal, where the decrease of $\langle\text{Pb-I-Pb}\rangle$ bond angle and Pb-I bond length exhibit an opposite influence on the band gap, *i.e.*, smaller bond angle results a widened band gap, while smaller bond length results a narrowed band gap. An abnormal double redshift behavior is reported in BAPI 2D perovskite for better solar absorbers. Structural variation will further impacts exciton dynamics. High pressure, as an effective tool, provides us deeper insight into the structure-property correlation from the atomic point of view, enabling us to optimize and engineer the functional properties (e.g., high-level bandgap narrowing) through

synthetic design for further photovoltaic and photoelectric applications of such 2D layered hybrid perovskite materials.

Chapter 7 summarizes all my current work and proposes new ideas for the future research in perovskite science area.

Chapter 2 Techniques and Optical Setups

2.1 High pressure technique

High pressure is a conventional tool to change the structures and electronic properties of materials⁷⁹. The corresponding pressure responses will facilitate the understanding of the structure-property relationship of materials⁸⁰. High-pressure conditions in the lab can be realized by using the diamond anvil cells (DACs), and the most widely used Mao-type symmetric DAC equipment is shown in Fig. 2.1. The DAC consists of two identical diamonds, and a gasket with a hole drilled in the center as the sample chamber. The diamonds act as anvils press inward on the sample between them by rotating the four screws⁸¹. The culet sizes of diamond anvils are around 500-600 μm and the hole sizes are around 200-300 μm , which enables the compression of sub-millimeter-sized piece of materials to extreme pressures, as demonstrated by the simple principle of $p = F/A$, where p is the pressure, F is the applied force, and A is the area. More specifically, the pressure is calibrated by using the ruby fluorescence and pressure transmitting medium is used to realize hydrostatic pressure condition.

The Mao-type DAC cell can be put under microscopes for optical measurements and is also designed for XRD measurements and conductivity measurements.

I utilized the Mao-type DAC for my high-pressure work as discussed in Chapter 5 and 6:

Two identical diamond anvils with a culet size of 500 μm were employed to generate pressure. A stainless-steel gasket was pre-indented to 50 μm in thickness with a drilled hole of 200 μm in diameter to serve as the sample chamber. The pressure

medium is silicone oil and a small ruby ball is loaded together with the MAPbBr_3 NCs (Chapter 5) and the exfoliated BAPI 2D perovskite flakes (Chapter 6).

Fig. 2.1 The Mao-type symmetric diamond anvil cells. All the components (left side) and schematic image (right side)¹¹.

2.2 Raman spectroscopy

2.2.1 Theory

Raman scattering is an example of inelastic light scattering, *i.e.*, energy exchanging (frequency, wavelength) between the incident light and an optical medium, as shown in Fig. 2.2 (a). Incident light with angular frequency ω_0 and wave vector k_0 interacts with the medium and losses energy to the medium (Ω and q), resulting in the scattered light with angular frequency ω_1 and wave vector k_1 . Such inelastic light scattering was first discovered by C.V. Raman from molecules in liquids, for which he was awarded the Noble prize in 1930. In general, the inelastic light scattering can be divided into two types: Stokes and Anti-Stokes scattering. All types of emission types can be described by the discrete vibrational energy states as shown in Fig. 2.2 (b). It is clear that there is no real absorption process, the incident photon excites the electrons into a virtual energy state (the virtual states are generally

located below any electronic state.), subsequently the excited electrons will relax into various vibrational states and generate vibrational/rotational modes in molecules or lattice vibrations in crystals. In phonon physics, Raman refers specifically to inelastic light scattering from optical phonons, *i.e.*, the lattice vibrations in solids. The Stokes Raman shift originates from a phonon emission, the scattered line shows energy of $h\nu_0 - h\nu_m$, while a phonon absorption for Anti-Stokes Raman shift ($h\nu_0 + h\nu_m$, the energy for scattered line). Although, both Stokes and anti-Stokes Raman scattering occur simultaneously in a molecular system, the intensity of Stokes scattering is much stronger as compared to the anti-Stokes scattering intensity. If the scattered photon energy keeps almost no change, resulting in Rayleigh scattering lines ($h\nu_0$). The correlated Raman spectrum as shown in Fig. 2.2 (c), the two opposite shifts actually refer to the Rayleigh scattered line and show in wavenumbers.

The Raman selection rule can be roughly explained in the molecular system, where the polarizability must be changed during the molecular vibration instead of oscillating dipoles, *i.e.*, the electron cloud of an atom or molecule is distorted from its original position and shape. The relationship between the induced dipole moment, P , and the electromagnetic field, E , is $P = \alpha E$, where the proportionality constant α is the polarizability. The polarizability represents the distortion of the electron cloud around a molecule, and is able to form instantaneous dipoles. The active Raman vibration should require the polarizability changes, which is described by the polarizability derivative, *i.e.*, $d\alpha/dQ$, where Q is the normal coordinate of the vibrations (e.g., r for a stretch, θ for a bend, etc). The selection rule for a Raman-active vibration, the polarizability derivative is non-zero, *i.e.*, $d\alpha/dQ \neq 0$. Scattering intensity is proportional to the square of the induced dipole moment, *i.e.*, to the

square of the polarizability derivative. The active Raman vibrational modes in CO₂ molecule originates from the polarizability changes, otherwise they are infrared active modes, as shown in Fig. 2.2 (d).

Fig. 2.2 (a) Schematic of inelastic scattering. (b) Energy level diagram of the Raman (Stokes and Anti-Stokes) and Rayleigh scattering in solids. (c) Raman spectrum. (d) The Raman activity of CO₂ vibrations.

2.2.2 Raman microscope system

Since the Raman scattering signal is extremely weak, only one photon could be scattered for 10^7 incident photons. A special technique should be developed to collect such weak signal and distinct it from the strongest Rayleigh signal. Raman spectroscopy is a useful analytical spectroscopic technique to collect Raman scattering signals generated from vibrational, rotational and low-frequency vibrational modes in an optical system.

As shown in Fig. 2.3, the WITec confocal Raman system that is used in our lab and the corresponding diagram of light path and work theory. The excitation source is usually a high-quality laser beam (e.g., 325 nm, 532 nm, 633 nm, etc.), which

interacts with a sample and excites the vibrations of chemical bonds. As a result, the scattered photons will loss or gain energy, shifting up or down from the original line position. Such energy shifts appearing in a Raman spectrum is unique, *i.e.*, ‘fingerprint’, for each chemical composition and can provide chemical and structural information of the material in a qualitative and quantitative way. Typically, the scattered light is collected with a lens and sent into a monochromator to disperse onto a charge-coupled device (CCD). The laser line (Rayleigh scattering) is rejected by a filter (notch filter, edge filter or band pass filter), to separating the weak inelastic Raman scattering signals. In my lab, we choose BragGrate Notch filters (BNF) with a bandwidth of 10 cm^{-1} and a large OD (>4) to access the ultra-low wavenumber region $\sim 10\text{ cm}^{-1}$. Diffraction grating with an 1800 grooves/mm is chosen in the spectrometer to well disperse the inelastic scattering light and realize a spectral resolution of 1.3 cm^{-1} .

Fig. 2.3 WITec alpha 300RAS confocal Raman system and the principle diagram of the optical path.

In my PhD thesis, I will study the structural properties of the hybrid lead halide perovskites by using Raman spectroscopy, *i.e.*, study the structural distortion under high pressure and low temperature, including the inorganic octahedra tilting in the

low-frequency region and the organic cation vibrations (hydrogen bonding) in the high-frequency region^{55, 82, 83}.

2.3 Photoluminescence

Photoluminescence (PL) is the light re-emission process after photoexcitation, involving excitation and relaxation process. As shown in Fig. 2.4, the schematic of PL process in a direct gap and indirect gap materials. The “direct” band gap means that the optical transitions between the valence and conduction bands in the materials are dipole allowed, *i.e.*, the momentum of electrons and holes is the same. Once a direct bandgap material absorbed photons with an energy larger than the bandgap energy, the electrons in the ground state will be excited to the high-energy states in the conduction band and generate holes in the ground state with the same k momentum, *i.e.*, the excitation process as described by the solid arrow in Fig. 2.4 (a). These excited electrons cannot remain in these excited states for long and lose energy via very fast electron-phonon coupling (~ 100 fs), relaxing into the bottom of the conduction band and the corresponding holes will relax to the top of valence band, *i.e.*, the relaxation process as described by the cascaded arrows in Fig. 2.4 (a). The relaxed electrons and holes are still non-equilibrium and need to further cool down upon recombination, forming a thermal distribution, *i.e.*, Fermi-Dirac distribution, as demonstrated by Fig. 2.4 (b). Only the electrons and holes occupied in these two shadows can be able to recombine finally and emit photons directly. The “indirect” bandgap means the photon emission in the materials requires a phonon assistance (emitted or absorbed) to match momentum conservation, because the conduction band minimum and valence band maximum are located at different points in the Brillouin zone (Fig. 2.4 (c)).

Fig. 2.4 Schematic diagram: (a) The photoluminescence process in a direct band gap semiconductor material after photon excitation at certain frequency ν_L . The electrons relax rapidly to the bottom of the conduction band and holes relax rapidly to the top of the valence band, forming a Boltzmann distribution before recombining by emitting photons. (b) The photoluminescence process in an indirect band gap semiconductor material. The photon emission in such materials requires a phonon assistance (emitted or absorbed) to match momentum conservation.

In general, the photoluminescence can be generated by the recombination of both excitons, free carriers, and defects in the semiconductor materials. It is important to study the emission mechanism in detail, *i.e.*, the relaxation and recombination process, by using steady-state photoluminescence spectroscopy combined with time-resolved photoluminescence spectroscopy.

In my PhD thesis, I will study the electronic and excitonic properties of the hybrid lead halide perovskites by using photoluminescence spectroscopy, *i.e.*, study the structure-optical correlation under high pressure and low temperature, including indirect to direct band transition upon cooling and multiple exciton emission under compression as well as dynamic properties. The steady-state photoluminescence measurement is conducted via the WITec confocal Raman system and the time-resolved photoluminescence measurement is implemented via home-made spectroscopy in my collaborator's lab.

***In situ* temperature-dependent Raman and PL measurements for MAPbBr₃ perovskite single crystal in Chapter 4.** Raman spectra were collected between 300 K and 80 K under a nitrogen gas flow cryostat equipped under WITec alpha 300RAS microscope. The 633 nm (red) line from a He-Ne gas laser was chosen for excitation with a power of 8 mW. The laser beam was focused on the sample using a long working distance 20X microscope objective (spot size $\sim 2 \mu\text{m}$). The backscattered Raman signal passed through two BraggGrate Notch Filters (BNF) centered at 633 nm with a bandwidth of 10 cm^{-1} and a large OD (> 4) to access the low frequency region. Spectra were collected with an Acton spectrometer with an 1800 grooves/mm diffraction grating (1.3 cm^{-1} resolution) and a thermo-electric cooled Andor CCD detector. For the PL measurement, a linearly polarized CW solid laser with the wavelength of 457 nm was used for excitation with a power of $30 \mu\text{W}$ and spectra were collected with an Acton spectrometer with an 150 grooves/mm diffraction grating ($\pm 0.5 \text{ nm}$ resolution).

***In situ* HP optical measurements for MAPbBr₃ perovskite NCs (Chapter 5) and BAPI 2D layered perovskite (Chapter 6).** Silicone oil was used as the pressure transmitting fluid. Steady-state absorption/PL and Raman spectra during compression and release were collected under WITec alpha 300RAS microscope. For the absorption measurement, a halogen lamp (15 V, 150 W, 3010 K) was chosen as the white light source. For the PL measurement, a linearly polarized CW solid laser with the wavelength of 457 nm was used for excitation with a power of $30 \mu\text{W}$, while a linearly polarized CW He-Ne gas laser (633 nm) with a power of 8 mW was chosen for Raman measurement. A long working distance 20 X microscope objective (spot size $\sim 2 \mu\text{m}$) was applied to focus the light beam on the sample. Both the absorption and PL spectra were dispersed by a 150 grooves/mm diffraction

grating (± 0.5 nm resolution), while an 1800 grooves/mm diffraction grating (1.3 cm^{-1} resolution) was chosen for the backscattered Raman signal collection. All optical signals are detected by a thermo-electric cooled Andor CCD detector. For time-resolved PL measurement, the 400 nm excitation pulses were generated via second harmonic generation (with a beta barium borate crystal) of the 800 nm output from the Coherent Libra regenerative amplifier (50 fs, 1 kHz) seeded by a Coherent Vitesse oscillator (50 fs, 80 MHz). The 400 nm laser is then passed through a 650 nm short pass filter to remove residual 800 nm photons in the beam. This beam is directed into a Nikon microscope and focused onto the sample (mounted in the diamond anvil cell) using a 10 $\times$ objective lens. The laser diameter on the sample is $\sim 100 \mu\text{m}$. The backscattered emission from the sample is collected using the sample objective and is passed through a 410 nm long pass filter to remove 400 nm excitation photons. The filtered emission is then directed into a monochromator (Acton, Spectra Pro 2300) followed by an Optronis OptoscopeTM streak camera system to obtain the PL kinetics. The ultimate resolution of this system at the fastest scan speed is ~ 10 ps.

2.4 Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) is a scientific analytical technique mainly used for structural identification of a powder or microcrystalline materials to provide information on unit cell dimensions. The fundamental principles of XRD is based on constructive interference of monochromatic X-rays and a crystalline material. The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the target sample. The interaction of the incident rays with the sample produces constructive interference

(bright spots). By measuring the angles where these bright spots occur, the various lattice spacings are determined by Bragg's Law, *i.e.*, $n\lambda=2d\sin\theta$.

The temperature-dependent *in situ* XRD patterns (Chapter 4) were accumulated using a Philips PANalytical X-ray diffractometer. Cu K $_{\alpha 1}$ radiation with a wavelength of 1.54 Å was used as the X-ray source. A helium gas flow cryostat controlled the temperature from 300 K to 80 K in 10 K intervals. Patterns were collected in θ -2 θ mode from 10° to 90° at a step size of 0.06°. This experiment is performed by my collaborator, Dr. B.M. Zhang and Prof. G.M. Chow, from National University of Singapore.

***In situ* HP-XRD measurement (Chapter 5 and 6)** was carried out on the B1 station at the Cornell High Energy Synchrotron Source (CHESS) with a monochromatic X-ray radiation of wavelength $\lambda = 0.485946$ Å (25.514 keV)⁸⁴. Experimental fitting of the X-ray synchrotron data was carried out using TOPAS 3 and employing the fundamental parameter approach. This measurement is done by my collaborator, Dr. S.J. Jiang and Prof. J.Y. Fang, from the State University of New York at Binghamton.

2.5 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique used to observe the features of very small specimens. This technology uses an accelerated beam of electrons to transmit through a very thin specimen (thickness <100nm) on a grid, forming an image from the interaction of the electron and the sample. The TEM image performs a significantly higher resolution, enabling to capture structure, crystallization and morphology information.

The series of TEM images of the MAPbBr₃ NCs collected from the DAC released at different pressure points (Chapter 5) were obtained by using a JEOL JEM2010F instrument. Samples were analyzed after orientation with a double tilting holder and the selected area electron diffraction (SAD) patterns were recorded. High-resolution images were collected using a high-contrast objective aperture of 20 mm, corresponding to a nominal point-to-point resolution of 0.17 nm. The experiment is performed by my collaborator, Dr. Y.N. Fang and Prof. T.J. White, from Nanyang Technological University, Singapore.

2.6 *Ab initio* calculations

The *ab initio* calculations, including geometry optimization, vibrational properties and molecule dynamics, used the projector-augmented wave (PAW)⁸⁵ method as implemented in the Vienna *Ab initio* Simulation Package (VASP)⁸⁶. The exchange correlation potential described by the Perdew, Burke and Ernzerhof (PBE) function was used within the generalized gradient approximation (GGA)⁸⁷. The energy convergence for the relaxation was chosen to be less than 10⁻⁵ eV/Å. The calculation part is performed by my collaborator, Dr. J.X. Yan, from Nanyang Technological University, Singapore.

***Ab initio* calculations for MAPbBr₃ perovskite single crystal (Chapter 4) and BAPI 2D perovskite single crystal (Chapter 6).** The phonon frequencies at the Γ point and Raman intensities were calculated within density-functional perturbation theory (DFPT)⁸⁸ as deployed in Phonopy⁸⁹. For MAPbBr₃ perovskite in the cubic phase, the Brillouin zone was sampled by a 6×6×6 k-point mesh using the Monkhorst-Pack (MP) method. For the tetragonal and orthorhombic polymorphs, a 4×4×2 MP k-point mesh was adopted. For BAPI 2D perovskite, the Brillouin zone

was sampled by a $3 \times 3 \times 1$ k-point mesh using Monkhorst-Pack (MP) method. The topological analysis of the bond critical points relating to the hydrogen bonds was performed using the AIM-UC program.⁹⁰ Taking account of nonlocal van der Waals interaction, we adopted the newly developed vdW density functional (vdW-DF2) in our study⁹¹.

Ab initio calculations for MAPbBr₃ perovskite NCs (Chapter 5). Taking account of nonlocal van der Waals interaction, we adopted the newly developed vdW density functional (vdW-DF2) in our study⁹². For the bulk phase, the Brillouin zone was sampled by a $6 \times 6 \times 6$ k-point mesh using the Monkhorst-Pack (MP) method. For the slab models, a $4 \times 4 \times 2$ MP k-point mesh was adopted. Each slab consists of two symmetric terminations to avoid spurious interaction between periodic slabs by dipole-dipole interactions. In addition, charge-balanced stoichiometric slabs are only considered by adjusting the number of surface atoms keeping above symmetry constraint in this study. For considered four surfaces, we constructed eight possible terminations as follows: MABr- and PbBr₂-terminated (010) surfaces, Br₂- and MAPbBr- terminated (110) surfaces, MABr- and PbBr₂- terminated (210) surfaces, and Pb- and MABr₃-terminated (111) surfaces. Unlike the (010) and (210) surface with two non-polar MABr- and PbBr₂- terminations, MAPbBr₃ (110) and (111) surfaces with the stoichiometric terminations will give rise to a monotonic raised microscopic electric field, which is compensated through an anomalous filling of the surface electronic states. At last, the comminution energy of each surface can be obtained through the following equation:

$$\gamma = \frac{E_{slab(A)} + E_{slab(B)} - nE_{bulk}}{4A}$$

where E_{slab} is the total free energy of the slabs with two complementary terminations (A and B) for each surface; and E_{bulk} is the total energy of the bulk MAPbBr₃ crystal.

Chapter 3 Sample Preparation

3.1 Preparation of 3D MAPbBr₃ perovskite single crystals

Single crystal MAPbBr₃ was prepared by precipitation from a halogenated acid solution^{93, 94}. In this process, 1.88g of lead (II) acetate was dissolved in 40 ml of 48 wt % acid HBr by heating in a water bath at ~ 90 °C. Subsequently, an additional 2 ml of HBr solution with 0.45 g of CH₃NH₂ (40 % soluble in water) was introduced. Large defect-free crystals were grown by cooling the aqueous solution from 90 °C to room temperature over 3 hours. The product was washed with acetone and dried overnight at 100 °C in a vacuum oven. Appreciable crystals were obtained via slow cooling from 90 to 50 °C over 3 days. The sample is synthesized by my collaborator, Dr. Y.N. Fang and Prof. T.J. White, from Nanyang Technological University, Singapore.

3.2 Preparation of MAPbBr₃ perovskite nanocrystals

MAPbBr₃ NCs were synthesized by the ligand-assisted re-precipitation method⁹⁵. The 5-aminovaleric acid was first converted into its ammonium salt (Br⁻NH₃⁺-(C₂H₂)₄-COOH) with a slight excess of hydrobromic acid (HBr). Subsequently, 0.5 ml of PbBr₂ (40 mM in DMF), 0.5 ml of MABr (40 mM in DMF), 95 μL of oleic acid and 3 μL of Br⁻NH₃⁺-(C₂H₂)₄-COOH were homogenously mixed and quickly injected into 10 ml of toluene under vigorous stirring at room temperature (RT). The resulting solution was centrifuged at 4000 rpm for 10 minutes and the precipitate collected and centrifuged again after redispersion in toluene. The sample is synthesized by my collaborator, Dr. T.M. Koh, from Nanyang Technological University, Singapore.

3.3 Preparation of BAPI 2D perovskite single crystals

Bulk crystals of BAPI were grown by following the procedure⁹⁶: 0.534 g (1.16 mmol) of PbI_2 was dissolved in 2 ml of 57 wt % aqueous HI solvent under flowing Ar with the temperature $\sim 90^\circ\text{C}$. At the same time, ~ 2.32 mmol of $(\text{C}_4\text{H}_9\text{NH}_2)\cdot\text{HI}$ was dissolved in 3 ml of concentrated HI solution in another tube. Upon cooling the solution from 90°C to -10°C at 2°C/h , the plate-like crystals with orange color are formed in Ar and dried at 80°C . The crystal surface degrades in ambient condition slowly, thus the glove box is preferred for sample storage. Thin layer of BAPI (down to monolayer, *i.e.*, 2.5 nm) can be exfoliated by using scotch tape following similar method for graphene exfoliation⁹⁷, then the BAPI flakes attached to the tape was transferred onto the diamond surface of DAC by a slow peeling. (Hexagonal boron nitride) hBN was mechanically exfoliated onto Polydimethylsiloxane (PDMS), which was adhered to a glass slide to facilitate operation⁹⁸. The alignment between the target BAPI sample and hBN was realized under microscope in glovebox. In the last, the PDMS was peeled off from hBN. The sample is synthesized and transferred by my collaborator, Dr. B. Liu, from National University of Singapore.

Chapter 4 Hydrogen Bonding Evolution during the Polymorphic Transformations in $\text{CH}_3\text{NH}_3\text{PbBr}_3$

4.1 Motivation

Hydrogen bonding is an electrostatic force in form of a dipole-dipole attraction, which occurs when a hydrogen atom bonded to a strongly electronegative atom. These bonds are generally stronger than dipole-dipole force, but much weaker than true covalent and ionic chemical bonds. In MA lead halide perovskites, *i.e.*, $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), hydrogen bonding plays a key role in intrinsic crystal structural stability⁹⁹ and excellent functional properties, as discussed in Chapter 1, where the interaction between organic MA cation and X-site inorganic anion, associated with order-disorder behaviors of the MA cations and numerous tilting patterns of the corner-connected inorganic PbX_6 octahedra¹⁰⁰⁻¹⁰². Therefore, exploring the structural and optical properties of MAPbBr_3 crystal is essential to maximize the utilization of this material in practical applications.

Recent theoretical and experimental studies suggest the hydrogen-bonding interactions of the MA cations and the “X-site” anions of the PbX_6 octahedra significantly contribute to fixing the phase transition points as a function of temperature^{99, 103, 104}. Density functional theory (DFT)⁹⁹, first-principles¹⁰³, and *ab initio* molecular dynamics¹⁰⁰ models demonstrate that the PbX_6 octahedra would not tilt without the contribution from hydrogen-bonding^{103, 105}. Several works have attempted to explore the role of MA dynamics in MAPbI_3 perovskite. In high-temperature (343 K) cubic MAPbI_3 , Bechtel *et. al*¹⁰⁶ calculated the MA cation orients preferentially along [100] guided by strong $\text{N-H} \cdots \text{I}$ interactions, while

Bakulin *et al.*²⁵ found that at 300 K MA reorients dynamically as a fast 'wobbling-in-a-cone' libration and a slow jump-like motion with respect to the PbI_3 lattice¹⁰⁰. For the tetragonal phase, the hydrogen-bonding network remains ambiguous with respect to the optimum MA orientation^{103, 107}. For example, Lee *et al.*¹⁰³ reported two distinct hydrogen-bonding interactions in tetragonal MAPbI_3 . In the low-temperature orthorhombic phase, MA cations are staggered, and the rotation around the C-N bond is hindered, by strong hydrogen-bonding⁹⁹. Experimentally, the orientation, location, and disorder of MA cations have been investigated by nuclear magnetic resonance (NMR) spectroscopy³⁶, quasi-elastic neutron scattering¹⁰⁸, and neutron powder diffraction (NPD).¹⁰⁹ These characterizations suggest the MA molecular mass center is slightly off the inorganic cage center and re-orientates rapidly in the tetragonal and cubic polymorphs, while the MA cations are fully ordered in the orthorhombic phase¹¹⁰. Current theory and experiment have not fully interpreted the MA dynamics in MAPbI_3 perovskite. As comparison, MAPbBr_3 system is more complex and endow three phases, which enables to explore the full physical picture of hydrogen-bonding evolution during the temperature-dependent polymorphic transformation. This evolution is universal for all hybrid organic-inorganic lead halide perovskites.

Raman spectroscopy is a powerful tool to characterize the temperature-dependent dynamics of MA vibrations and rotations inside the PbX_3 inorganic cage, and to elucidate the formation and strength of H bonds with Br ions. Previous Raman measurements focused on the assignment of vibrational modes, where the region below 200 cm^{-1} was attributed to the inorganic cage vibrations (similar to the low-

frequency Raman spectrum of inorganic CsPbBr_3)¹¹¹ and the organic cations contribute to spectral frequencies greater than 200 cm^{-1} ^{49, 112}.

In this study, Raman scattering and XRD of MAPbBr_3 were used to investigate the MA cation dynamics as a function of temperature. It is the H-bond formation between Br and H of the $\text{CH}_3/\text{NH}_3^+$ groups and the weakening of C-H /N-H bonds, that causes the $\text{CH}_3/\text{NH}_3^+$ vibrations to narrow and red shift. The Raman spectra demonstrate that the phase transition at $\sim 140\text{ K}$ corresponds with H-bond formation between the CH_3 group and the Br ions that locks the CH_3 group in the inorganic cage, which is accompanied by NH_3^+ group re-orientation and $\text{H}_\text{N} \cdots \text{Br}$ bond weakening. Low-temperature diffraction is consistent with the phase transition temperatures derived from Raman spectroscopy. Extensive *ab initio* calculations are consistent with the experimental observations and provide coordinates for the light atoms, including H. As expected, H bonds vary across the polymorphs with $\text{Hc} \cdots \text{Br}$ forming only in the orthorhombic phase.

4.2 Results and discussions

4.2.1 Phase transformations and Raman mode assignments

Fig. 4.1 (a) Low-frequency Raman spectra of an MAPbBr₃ perovskite single crystal (optical image shown as inset) at various temperatures. (b) Lattice parameters and phase transitions determined from the Rietveld refinement of temperature-dependent (300 K - 80 K) XRD patterns. The discontinuity in the lattice constant between 120 and 140 K is due to the coexistence of the tetragonal and orthorhombic polymorphs.

Fig. 4.1 (a) shows the low-frequency Raman spectra of MAPbBr₃ single crystals (optical image in the inset and sample characterization in Figure 4.2) were collected with the temperature between 300 and 80 K. At room temperature, Raman bands are indistinct, but < 230 K, a broad low-intensity feature appears at ~70 cm⁻¹, due to the partially dynamic disorder of the MA cations. Peaks are better resolved below 140K, instead of two broad humps, coinciding with the tetragonal-to-orthorhombic phase transition where both the CH₃ and NH₃⁺ groups are locked (to be discussed later). The vibrational spectra in three distinct temperature ranges, confirm different ordering states in the polymorphs. The Raman spectra correlate well with temperature-dependent *in situ* powder XRD results (Fig. 4.1 (b)), where the cubic (*Pm* $\bar{3}$ *m*) to tetragonal (*I4/mcm*) transition takes place at ~ 230 K, the orthorhombic (*Pnma*) transition is at ~ 140 K, and the tetragonal II (*P4/mmm*) and orthorhombic phase coexist between 120 and 140 K (Fig.3.3) based on previous dielectric measurement¹¹³.

Fig. 4.2 Characterization of MAPbBr₃ single crystal sample at room temperature. (a) X-ray diffraction pattern of MAPbBr₃, which has been indexed assuming cubic symmetry of $Pm\bar{3}m$. (b) Raman scattering of MAPbBr₃ excited by 633 nm laser and (c) Photoluminescence of MAPbBr₃ excited by 457 nm laser.

Fig. 4.3 Whole pattern fitting between calculated (red line) and experimental (black line) diffraction profiles for perovskite at 140 K. The discontinuity in the lattice constant between 120 and 140 K is due to the coexistence of the tetragonal and orthorhombic polymorphs.

Fig. 4.4 shows the experimental spectra (the solid lines) and calculated phonon dispersion (bars) for three polymorphs, demonstrating that two low-temperature phases have more phonon bands, due to the splitting of degenerate modes at lower symmetry, and the quadrupling of the tetragonal and orthorhombic unit cell volume, compared to the cubic phase. The Raman frequencies below 200 cm⁻¹ are dominated

by the PbBr_3 inorganic cage vibrations^{114, 115}. The high-frequency Raman spectra reflect MA re-orientation as temperature changes, which is a marker of the degree of steric hindrance experienced. The agreement between theory and observation enables the assignments and dynamics exploration of MA vibrations. The Raman band at 300 cm^{-1} belongs to the MA torsional mode (τ (MA)), while two rocking modes are found at 913 cm^{-1} (ρ_1 (MA)) and 1247 cm^{-1} (ρ_2 (MA)) along with the C-N stretching mode at 966 cm^{-1} (ν (C-N)). The modes, located in the high-frequency regions above 1300 cm^{-1} , are associated with the symmetric (*s*)/asymmetric (*as*) bending (δ) and stretching (ν) of the CH_3 and NH_3^+ groups.

Fig. 4.4 Raman band assignments for an MAPbBr_3 single crystal. Full vibrational spectra are given for the cubic (dark cyan line), tetragonal (dark pink line) and orthorhombic (grey line) phases. The corresponding calculated phonon dispersion is shown left insets. The representative

MA molecular rotations are reported in the right insets. τ : torsion; ρ : rocking; δ : bending; ν : stretching; s : symmetric; as : asymmetric.

4.2.2 Temperature-dependent Raman spectra in the high-frequency region

Fig. 4.5 (a) shows the temperature-dependent rocking modes and the C-N stretching mode, with a continuous blue shift in passing from the cubic to tetragonal phases. It reflects contraction of the inorganic cages with decreasing temperature. More importantly, a sudden lowering in frequency and a considerable narrowing in linewidth (Fig. 4.6 (a)) for ρ_1 (MA) and ν (C-N) modes in the orthorhombic phase, indicate that the C-N bonds have stretched and weakened, while the degrees of freedom are restricted, compared to the tetragonal phase. (The C-N bond length will be considered quantitatively later.) These two modes involve stretching of the C-N bond, while no significant change in frequency is found for the ρ_2 (MA) mode that is correlated to the rigid body rocking of the C-N bond (Fig. 4.5 (b)).

Fig. 4.5 Temperature-dependent Raman spectra for MAPbBr₃. (a) Evolution of MA vibrations from room temperature (300K) to low temperature (80K). Insert: Raman shifts vs temperature for C-N stretching mode (ν (C-N)) of 966 cm⁻¹ (300K) and two MA rocking modes (ρ (MA)) of 913 cm⁻¹ and 1247 cm⁻¹ (300K). The dotted lines mark the phase transition temperatures. (b)

The corresponding representative modes are reported in the right panel, where the red cones are the atomic displacements and arrows denote molecular mode.

Fig.4.6 Temperature dependences of full width at half maximum (FWHM) of the vibrational bands at: 913 and 1247 cm⁻¹; 966 cm⁻¹; and 2826 and 2966 cm⁻¹, associated with two ρ (MA) modes; ν (C-N) mode; ν_s (NH₃⁺) and ν_s (CH₃) modes, respectively. The experimental data collected between 300 K and 80K.

Fig. 4.7 (a) shows the temperature-dependent Raman modes of the respective CH₃ group and NH₃⁺ group, are readily correlated with the hydrogen-bonding dynamics. The asymmetric bending modes appear at δ_{as} (CH₃) = 1426 cm⁻¹ and δ_{as} (NH₃⁺) = 1590 cm⁻¹, while the symmetric stretching modes are observed at ν_s (CH₃) = 2826 cm⁻¹ and ν_s (NH₃⁺) = 2966 cm⁻¹. In agreement with calculations, the CH₃ and NH₃⁺ groups display a similar red shift in the cubic and tetragonal polymorphs, while in the orthorhombic phase show an opposite trend (Fig. 4.7 (b-c)). The ν_s (CH₃) Raman mode is broad in the cubic and tetragonal polymorphs (Fig. 4.6 (b)), indicating the CH₃ group in the inorganic cage possesses high freedom. The blue shift for NH₃⁺ group and the red shift for CH₃ group in the orthorhombic phase, indicating the hydrogen-bonding of H_N ... Br becomes weaker when H_C ... Br bonds form. Besides, Raman modes of the NH₃⁺ group are more pronounced than those of the CH₃ group due to the relatively strong H_N ... Br strength compared to that of H_C ... Br¹⁰⁰.

Fig. 4.7 Temperature-dependent the Raman spectra of single crystal MAPbBr₃. (a) Evolution of C-H and N-H asymmetric bending modes and symmetric stretching modes between 300 and 80 K. (b) Raman shifts for C-H asymmetric bending modes ($\delta_{as}(\text{CH}_3)$) and N-H asymmetric bending modes ($\delta_{as}(\text{NH}_3^+)$) as a function of the temperature. (c) Raman shift for C-H symmetric stretching ($\nu_s(\text{CH}_3)$) and N-H symmetric stretching ($\nu_s(\text{NH}_3^+)$) as a function of the temperature. The dotted lines mark the phase transition temperatures.

4.2.3 *Ab initio* calculations examined the states of hydrogen-bonding

Hydrogen-bonding plays an important role in stabilizing octahedral tilting and triggering the polymorphic transitions. The distinct chemical environments for MA orientations were calculated for each symmetry and the most stable state of the hydrogen-bonding between the MA and PbBr₃ cage determined (the top panel in Fig. 4.8). *Ab initio* calculations are adopted to simulate the MAPbBr₃ atomic structure in each polymorph. The unit cell volumes refined by powder XRD at three representative temperature points were used as the input parameters and the lattice parameters and atomic geometry were allowed to relax at fixed unit cell volumes by taking delocalized van der Waals (vdW) interactions into consideration. This approach avoids artefacts the induced by symmetry constraints¹⁰³.

At room temperature, the $a^0a^0a^0$ PbBr_6 tilting configuration in Glazer notation¹¹⁶ for the relaxed cubic ($Pm\bar{3}m$) structure aligns MA cations along $[110]$ (the top panel in Fig. 4.8 (a)). Three high-symmetry orientations of the molecules along $[010]$, $[110]$ and $[111]$ directions indicate that the CH_3NH_3^+ molecules show preferential alignment along $[110]$ in agreement with neutron diffraction measurements⁵². Note that the MA molecular mass center is displaced slightly from the inorganic cage center, leading to a lower-symmetry local structure, which attributes to the formation of the hydrogen-bonding between the NH_3^+ group and PbBr_6 octahedra, while the CH_3 group does not form hydrogen-bonding. Upon cooling, the tetragonal $I4/mcm$ structure $a^0a^0c^-$ stabilises (the top panel in Fig. 4.8 (b)) and the orthorhombic $Pnma$ structure $a^-b^+a^-$ (the top panel in Fig. 4.8 (c)) appears below 140 K^{52, 114}.

Fig. 4.8 The simulated cubic (c), tetragonal (b) and orthorhombic (a) periodic structures showed along arbitrary axis (the top panel). The corresponding unit cells (outlined by the black solid

lines) presented are extracted from these three optimized structures (the middle panel). The corresponding structures viewed along the *c*-axis) with the calculated bond length of H $\cdots$ Br (the bottom panel).

Indeed, the shorter distance (~ 2.46 Å and ~ 2.47 Å) between H_N and axial Br_A (or equatorial Br_E) compared to that between H_C and surrounding Br atoms (>3.00 Å) in the cubic phase makes the MA molecular mass center deviate from the inorganic cage center and primarily orient along [110], leading to a pseudocubic unit cell (the middle and bottom panel in Fig. 4.8 (a)). Hence in this phase, the H_N atoms form hydrogen bonds with the Br ions while the H_C atoms do not. In the tetragonal phase, two of the H_N atoms form shorter hydrogen bonds H_N(2) /H_N(2') $\cdots$ Br at ~ 2.36 Å, while the other H_N atom is equidistance between the Br ions of two neighbouring cages with hydrogen bonds length (H_N(1) /H_N(1') $\cdots$ Br) of ~ 2.74 Å, which directly correlates to the opposing out-of-plane rotation of two neighbouring octahedra, resulting in a $a^0a^0c^-$ tilting system^{117, 118} (the middle and bottom panel in Fig. 4.8 (b)). There is no hydrogen-bonding for the H_C atoms in the tetragonal phase. Below 140 K, the distance between H_C and Br shortens to ~ 2.85 Å, and these newly formed hydrogen bonds draw the MA cation towards to the CH₃ end, while three almost equivalent H_N $\cdots$ Br bonds of ~ 2.40 Å pull the MA cation towards to the NH₃⁺ end, leading to a lengthening of the C-N bond from 1.490 Å in the tetragonal phase to 1.492 Å in the orthorhombic phase (the middle and bottom panel in Fig. 4.8 (c)). This result is counter intuitive and perhaps surprising, because the unit cell volume decreases upon cooling and the C-N bonds should have strengthened accordingly. This weakening of the C-N bonds is a clear manifestation of the H_C $\cdots$ Br formation, which leads to the lowering of Raman frequency for both the ρ_1 (MA) and ν (C-N) modes (Fig. 4.5 (a)). Besides, the formation of both H_C $\cdots$ Br and H_N $\cdots$ Br bonds

leads to both in-plane and out-of-plane rotations of the inorganic cages, *i.e.*, the $a^-b^+a^-$ three-tilt systems^{117, 118}.

Fig. 4.9 The calculated hydrogen-bonding energy of the $H_N \cdots Br$ and $H_C \cdots Br$ bonds for the $MAPbBr_3$ polymorphs.

To quantitatively evaluate the hydrogen-bonding strength between the H atoms and Br ions, the hydrogen-bonding energy was calculated (Fig. 4.9) from the kinetic energy density using $E_{HB} = 0.429G(r_{BCP})$ based on the electron density $\rho(r_{BCP})$ and the corresponding Laplacian of charge density $\nabla^2\rho(r_{BCP})$ at all the relevant bond critical points (BCPs) using $G(r_{BCP}) = \frac{3}{10}(3\pi^2)^{2/3}\rho(r_{BCP})^{5/3} + \frac{1}{6}\nabla^2\rho(r_{BCP})$ ^{119, 120}.

Based on accepted hydrogen-bonding criteria (i) $0.002 < \rho(r_{BCP}) < 0.034 \text{ a.u.}$ and (ii) $0.024 < \nabla^2\rho(r_{BCP}) < 0.139 \text{ a.u.}$ at the BCPs, the calculations for the tetragonal and cubic phases show hydrogen-bonding interactions are dominated by H atoms in the NH_3^+ group, while both the $H_C \cdots Br$ and $H_N \cdots Br$ bonds are significant for the orthorhombic phase. In particular, the total hydrogen-bonding energy of $H_N \cdots Br$ increased from 0.326 eV in the cubic phase to 0.473 eV in the tetragonal phase, leading to weakening of the N-H bond and the red shift of N-H Raman modes. These calculations also demonstrate that although there are no hydrogen bonds between

$H_C \cdots Br$ in these two polymorphs, shrinkage of the inorganic cages enhances the vdW interactions and softens the C-H bond. By contrast, the total hydrogen-bonding energy of $H_N \cdots Br$ in the orthorhombic phase decreases slightly to 0.412 eV, while the newly formed $H_C \cdots Br$ bonds contribute to a total hydrogen-bonding energy of 0.162 eV, resulting in a red shift of the C-H vibrational modes and a blue shift of the N-H vibrational modes.

4.2.4 Hydrogen-bonding influence on the electronic properties

Based on our temperature-dependent Raman spectra and theoretical results, the rotation of MA and tilting of $PbBr_6$ octahedra are ascribed to the hydrogen-bonding between the H atoms of CH_3/NH_3^+ and Br atoms. The different hydrogen-bonding interactions between the H and Br in those three phases, increase the structural stability and lead to the structural transitions with the Pb-Br bond length and Br-Pb-Br bond angle changing, which further influence the electronic structures near the bandgap of hybrid perovskites as the structural factor¹²¹⁻¹²³. As discussed in section 1.3, the band gap of $MAPbBr_3$ is determined by the distortion of $PbBr_3$ inorganic lattice, where the valence band maximum (VBM) consists of the anti-bonding coupling of the *s* orbital of Pb and the *p* orbital of Br, and the conduction band minimum (CBM) is mainly determined by the non-bonding *p* orbital of Pb.

Fig. 4.10 Opto-electronic properties during phase transformation. (a) Temperature-dependent PL spectra of MAPbBr₃ from 300K to 80K. (b) Integrated PL emission intensity as a function of temperature. (c) Evolution of PL peak position (the solid diamonds) and calculated band gap E_g (the solid circles) as a function of the temperature. (d) The magnification of the band structures around the bandgap at three representative temperature point shows the transition from indirect bandgap to direct bandgap during cooling. The red dots show the valence band maximum (VBM) and conduction band minimum (CBM).

To explore the role of various hydrogen-bonding behaviors on the opto-electronic properties of MAPbBr₃ during cooling, we have performed both the temperature-dependent PL measurement on MAPbBr₃ perovskite from 300K to 80K and the first-principle calculations of the electronic structures for various polymorphs, as shown in Fig. 4.10. At each representative temperature point, we adopted the refined unit cell volume (Fig. 4.11) as the starting parameter based on our powder XRD data and then optimized the atomic geometry. Fig. 4.10 (b) shows the PL intensity is enhanced (~60 times in maximum) in low-temperature tetragonal phase (orange spheres) and orthorhombic phase (cyan spheres), while no enhancement in cubic

phase (dark pink spheres). PL emission peak (solid diamonds) shows an unusual blue shift in each phase and a red shift between phase transformation with increasing temperature, which matches well with the calculated bandgap E_g (solid circles) evolution (Fig. 4.10 (c)), suggesting the bandgap narrowing during each phase transition upon heating (Fig.4.10 (d)). More significantly, the red shift is more obvious during orthorhombic-tetragonal phase transition compared to that during tetragonal-cubic phase transition, which originates from the more distorted crystal structure of MAPbBr₃ in orthorhombic phase due to the severe in-plane and out-of-plane tilting of PbBr₆ octahedra with the forming of H_C $\cdots$ Br bonds in orthorhombic phase. The much smaller Pb-Br-Pb angle in orthorhombic phase weakens the interaction between the *s* orbital of Pb and the *p* orbital of Br that further pushes down the top of valence band, while the CBM is non-sensitive to bond angle, resulting in a much wider band gap in orthorhombic phase. Inside each phase, the Pb-Br bond length decreases upon cooling, leading to an enhanced interaction between the *s* orbital of Pb and the *p* orbital of Br that further lifts up the top of valence band, resulting in a narrowing in band gap in each phase. Through focusing on the bands around the bandgap at each representative temperature point, we found that the cubic phase is indirect bandgap instead of the direct bandgap feature in the other two low-temperature phases, accounting for the PL enhancement in low-temperature phases. The barrier in cubic phase is around 10 meV, smaller than $k_B T$ and the previous reported values (20 meV)¹⁰², attributed to the adopted “real” unit cell volume in our study instead of the ground value at 0 K. Given that the hydrogen-bonding interactions can affect the order-disorder behaviors of the CH₃NH₃⁺ cations in the cages, leading to specific optoelectronic properties and device applications, we suggest that hybrid perovskite in cubic phase (negligible hydrogen-bonding

interactions and random CH_3NH_3^+ cations) is good for solar cell applications, while enhanced light-emitting properties (strong hydrogen-bonding interactions and locked CH_3NH_3^+ cations with ordered arrangement, as well as the direct bandgap feature) in low temperature orthorhombic phase.

Fig. 4.11 Unit-cell volume determined from the Rietveld refinement of temperature-dependent (300 K - 80 K) XRD patterns.

4.3 Conclusions

In summary, a comprehensive and direct experimental-theoretical approach is provided here to identify the dynamics of the MA orientations and the hydrogen-bonding in MAPbBr_3 during temperature-dependent polymorphic transformation. Excellent correlation between Raman spectroscopy, powder X-ray diffraction and ab initio calculation resolved the different types of H-bonds between MA and the PbBr_3 inorganic cage in the cubic ($Pm\bar{3}m$), tetragonal ($I4/mcm$) and orthorhombic ($Pnma$) phases. The key outcome is that $\text{Hc} \cdots \text{Br}$ becomes significant only in the low temperature orthorhombic polymorph, which rationalizes the state of the MA cations and the concomitant tilting of PbBr_6 octahedra with the consequent

dynamical change of the band structures, *i.e.*, indirect bandgap to direct bandgap transition. Developing a quantitative understanding of the strength and orientation of the hydrogen-bonding of the MA cations is the first step towards optimizing the optoelectronic properties of this class of materials for solar cell and related applications.

Chapter 5 High Pressure-Induced Comminution and Recrystallization of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Nanocrystals

5.1 Motivation

Under sufficient pressure the surface states¹²⁴, crystallography¹²⁵⁻¹²⁷, electronic properties^{84, 128, 129} and carrier dynamics⁷ of materials alter significantly. In particular, the compression of appreciable hybrid perovskite single crystals has been studied intensively. Wang *et al.* described pressure-induced phase transformations and anomalous band gap evolution in MA lead bromide $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ⁴², while Karunadasa *et al.* and Zhou *et al.* studied electronic and optical variants of hybrid 3D perovskites^{41, 42, 130} and Cu-Cl 2D perovskites^{80, 131}. More recently, Kong *et al.* achieved unprecedented carrier-lifetime prolongations of 70% to ~100% in $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals by applying ~0.3 GPa⁷. These changes in symmetry, bandgaps and carrier lifetimes may be caused by the PbX_6 octahedral tilting or the defects arising from amorphization^{3, 7, 130}. In most large crystals the physical and chemical properties are restored during pressure release.

Nanocrystals respond specifically to pressure with respect to phase progression^{125, 132, 133}, coherent crystal domain size¹³⁴, particle agglomeration¹³⁵ and morphology^{136, 137}. For example, distinct textural coalescence creates (meta)stable compounds in metallic nanoparticle (NPs) and semiconductors including silver/gold¹³⁸⁻¹⁴⁰, CdSe^{141, 142} and PbS/Pt^{141, 143}. Alteration of carrier dynamics in CdTe nanocrystals¹⁴⁴ and CsPbBr_3 quantum dots (QDs)¹⁴⁵ has also been reported. Whereas, the series of phase transformations during compression in bulk hybrid perovskites would perform a

different pressure response on the nano-counterparts. This work is concerned with the structural mechanism behind the pressure-induced morphological modification in hybrid perovskite NCs, demonstrating that the structural phase transition of this hybrid perovskite crystals drives a comminution and recrystallization of MAPbBr₃ NCs as large thin nanoplates (NPs). The harvesting nanocrystalline variants, *i.e.*, MAPbBr₃ NPs, are examined to show good viability with improved stability and functionality.

To address the hybrid perovskite nanomaterials' response to pressure, a high-pressure technique using diamond anvil cells (DACs) is applied on MAPbBr₃ NPs (space group: $Pm\bar{3}m$) with size of ~10 nm for the first time. Mild pressure (~2 GPa) leads to comminution along (210)_{cubic}/(301)_{ortho} planes with the phase transformation to orthorhombic ($Pnma$), and the large (~100 nm) thin (<10 nm) nanoplates form via amorphization and recrystallize at higher pressures (~4 GPa). The comminution along (210)_{cubic} is due to PbBr₆ octahedral tilting as an inevitable consequence of adopting orthorhombic symmetry ($Pnma$). Subsequently, longer-range atomic order of perovskite is lost prior to reconstructive transformation as nanoplates that exhibit blue-shifted photoluminescence (PL) (~5 nm) with enhanced intensity (~15-fold) and shorter carrier lifetimes ($\sim 7.6 \pm 0.5$ ns) compared to the original NPs. These pressure-modified perovskites may prove advantageous for nanolaser and light-emitting diode applications¹⁴⁶.

5.2 Results and discussions

5.2.1 Pressure-induced phase transitions and octahedra tilting

The MAPbBr₃ NCs synthesized by ligand-assisted re-precipitation have an average diameter of ~10 nm (Fig. 5.1 (a)) and are highly crystalline (Fig. 5.1 (b)). The DAC diamond flat was loaded by direct drop-casting of NCs dissolved in toluene followed by solvent evaporation (Fig. 5.1 (c)). *In-situ* high-pressure synchrotron powder XRD monitored lattice evolution under compression (up to ~11 GPa) and release (Fig. 5.1 (d)). At ambient pressure, the MAPbBr₃ is cubic $Pm\bar{3}m$ ($a = 5.8725$ Å). With increasing pressure, the Bragg reflections progressively shift to higher diffraction angles (unit cell volume reduction) in the pressure range of 0.11 - 0.99 GPa as expected. At 0.99 GPa, two additional low intensity reflections appear at $2\theta \sim 7.6^\circ$ and 9.0° indicating a pressure-induced phase transition. Pawley fitting is consistent with the $Im\bar{3}$ ($a = 11.5600$ Å) polymorph with a doubled cell edge compared to the $Pm\bar{3}m$ phase. As pressure rose to ~2.41 GPa the reflection near 9.8° split indicative of the orthorhombic ($Pnma$, $a = 7.978$ Å, $b = 11.4507$ Å, $c = 8.001$ Å) modification. Above ~4.06 GPa a broad background (centered at $\sim 10.5^\circ$) appeared, and the intensities of all diffraction reflections decreased due to amorphization, while the $(001)_{\text{cubic}}$ peaks are still observable up to ~11 GPa, indicative of partially periodic atomic order. Upon decompression, the amorphous MAPbBr₃ returned to the cubic $Pm\bar{3}m$ phase with nearly the same unit cell parameters ($a = 5.8740$ Å).

Fig. 5.1 Pressure-induced phase transition and structural distortion. (a) A typical LR-TEM image of MAPbBr₃ perovskite NCs with average diameter of ~10 nm. (b) Plan-view HR-TEM image taken along [111] zone axis with the FFT pattern (inset) showing single-crystalline nature of the NCs. (c) Overall schematic of the diamond-anvil cell (DAC) for high-pressure measurements and the zoomed-in image of DAC showing the model of initial MAPbBr₃ NCs. (MA model is simplified.) (d) The integrated spectra from HP-XRD images at various pressures. (e) Refined crystal structures in three phases, demonstrating PbBr₆ octahedra tilting and MA cations ordering during phase transformation. (f) Optical micrographs of the piezochromic phenomenon during phase transition.

In summary, these observations are consistent with $Pm\bar{3}m$ (cubic) $\rightarrow$ $Im\bar{3}$ (cubic) $\rightarrow$ $Pnma$ (orthorhombic) transitions and partial amorphization beyond ~4.0 GPa, as reported for large MAPbBr₃ crystals^{3, 44}. The corresponding atomic models are shown in Fig. 5.1 (e) and the fitted lattice parameters are presented in Fig. 5.2. In the pristine perovskite ($Pm\bar{3}m$), PbBr₆ octahedral topology creates a regular cubic network, while the MA cation (with C_{3v} molecular symmetry) is disordered over 12 $\langle 110 \rangle$ directions to satisfy O_h symmetry¹⁴⁷. Within the octahedra, the Pb-Br bond shortens (Fig. 5.3 (a)) under pressure, and the Pb-Br-Pb bridging angle (Fig. 5.3 (b)) progressively becomes more acute beyond 0.99 GPa. The Br atoms are displaced

from the special Wyckoff $3c$ sites to occupy $24g$ sites consistent with PbBr_6 octahedra with $a^+a^+a^+$ Glaser tiltings of equal magnitude about all the pseudocubic axes¹⁴⁸. The unit cell volume reduction (Fig. 5.3 (c)) and the tilting of PbBr_6 (Table 5.1) induce the $Im\bar{3}$ transition. By further increasing the pressure, the rigid PbBr_6 octahedra adopt $a^+b^-b^-$ tilting system ($Pnma$) (Table 5.1)¹⁴³ accompanied with orientational ordering of MA cations due to hydrogen-bonding interaction¹⁴⁹. The phase transitions can also be evident by the NC piezochromism (Fig. 5.1 (f)).

Fig. 5.2 The lattice parameters evolution and phase diagram of MAPbBr₃ NCs as a function of pressure. (a) Lattice parameters of MAPbBr₃ NCs with pressure from 0 GPa to 4.5 GPa. (b) Lattice parameters of MAPbBr₃ NCs upon decompression to ambient pressure. The lattice parameters are determined from the Rietveld refinement of HP-XRD patterns. The grey dashed line represents the phase transition. During compression, cell parameters of pseudo-cubic (a_0 , b_0 , c_0) change considerably, and the two discontinuities at around 0.7 GPa and 2.0 GPa corroborate two phase transitions. The dispersed distribution of c lattice parameter after ~4 GPa, indicates the onset of amorphization. After release pressure, all the lattice parameters spring back to original ones in ambient condition.

* There are two Br positions (4c and 8d) in the $Pnma$ structure.

Fig. 5.3 The evolution of the Pb-Br bond length (a) and Pb-Br-Pb bond angle (b) as the function of pressure. In the $Pm\bar{3}m$ cubic phase, the bond length shortens a lot with the Pb-Br-Pb bond angle of 180° ; In the $Im\bar{3}$ cubic phase, the Pb-Br-Pb bond angle decreases a lot compared to the Pb-Br bond length; In the $pnma$ orthorhombic phase, there are two Br positions ($4c$ and $8d$), leading to both of the Pb-Br bond length and Pb-Br-Pb bond angle changing in complex ways.

Table 5.1. Variation in tilting angles of $PbBr_6$ as a function of pressure.

Space group	$Pm\bar{3}m$	$Im\bar{3}$			$Pnma^*$			
Pressure (GPa)	< 1	0.99	1.15	1.62		2.41	2.99	3.29
Tilt ($^\circ$)	0	6.1	7.445	10.535	θ	11.03	10.37	9.40
					φ	10.55	11.55	12.74
					Φ	15.22	15.47	15.79

* θ , φ and Φ represent rotations of $PbBr_6$ octahedron about the pseudo-cubic $[110]_{cubic}$, $[001]_{cubic}$, and $[111]_{cubic}$ axes, respectively^{150, 151}.

5.2.2 High-pressure-induced comminution and recrystallization of $MAPbBr_3$ perovskite NCs.

The evolution of NC morphology was examined by TEM of the retrieved $MAPbBr_3$ products, where compression was released from 0.75 GPa, 2.23 GPa, 6.5 GPa and 11 GPa (Fig. 5.4). At ~ 0.75 GPa the NCs deform and agglomerate to form clusters (Fig. 5.4 (a,b)), but after treatment at ~ 2.23 GPa (Fig. 5.4 (c,d)) comminution leads to nanoslices with the ribbon-like projections appearing within rectangular boundaries. The selected area electron diffraction (SAED) pattern (inset) demonstrates the nanoslices are single crystals. Moreover, the high-resolution TEM image further supports the single-crystalline nature of these nanoslices. The lattice fringes ($\sim 0.26 \pm 0.02$ nm) observed in this image agree well with the d-spacing of the $(210)_{cubic}$ lattice planes in $Pm\bar{3}m$ phase and confirm the comminution on these lattice planes. From ~ 6.5 GPa imperfect nanoplates with evident extended defects

are recognized (Fig 5.4 (e,f)), while large homogeneous crystals appear after ~11 GPa release (Fig. 5.4 (g,h)). Taken together, the microscopy suggests that pressure induces comminution and recrystallization of MAPbBr₃ NCs follows (Fig. 5.4 (i)):

① deformation and division of the NCs into nanoslices that expose fresh interfaces (210)_{cubic} during the cubic-orthorhombic transformation to create 1D ribbon-like TEM projections (Fig. 5.4 (d)); then ② the nanoslices with capping ligands off via amorphization, recrystallize as single-crystalline NPs (Fig. 5.4 (h)). In MAPbBr₃ NCs, the pressure-induced cubic-orthorhombic phase transition along with the complex tilting of PbBr₆ octahedra and the orientational ordering of MA cations drives the morphological modification under compression, in contrast to the pressure-induced direct self-assembly of CsPbBr₃ NCs only involving the cubic aristotype¹⁴⁵.

Fig. 5.4 Pressure-induced comminution and recrystallization of perovskite NCs. (Left column) A series of LR-TEM images of MAPbBr₃ nanostructures obtained at representative released pressures, correlated to different growth stages of MAPbBr₃ NCs. (Right column) A series of HR-TEM images of the corresponding MAPbBr₃ nanostructures and FFT patterns from selected sample regions (Inset). (i) The pressure-driven structure transformation pathway of MAPbBr₃ NCs: ① Pressure-induced deformation and comminution of NCs into nanoslices along (210) planes. ② Amorphization and recrystallization sintering of nanoslices into large thin nanoplates along with interface relaxation.

5.2.3 Understanding of pressure-induced comminution from atomic-level.

Fig. 5.5 Understanding of pressure-induced comminution from atomic-level. (a) During the cubic to orthorhombic phase transformation, the PbBr_6 octahedra tilt along a^+b^- system. Red arrows represent the rotation directions. MA molecules are filled between (301) planes with ordered configuration, corresponding to (210) planes in cubic phase. (b) The calculated $(210)_{\text{cubic}}$ and $(301)_{\text{ortho}}$ surface slab models.

The structural mechanism underlying NC comminution under pressure, can be understood through analysis of the atomic structures. Fig. 5.5 (a) shows the structural relationship between the cubic and orthorhombic phases. The $(301)_{\text{ortho}} \equiv (210)_{\text{cubic}}$, are nearly co-incident lattices ($d \sim 0.26 \pm 0.02$ nm) (Fig. 5.4 (d)). The PbBr_6 octahedra in the orthorhombic polymorph are tilted in the same (in-plane tilt a^+) and opposite (anti-plane tilt b^- and c^-) sense¹⁴⁸, and the Pb and Br atoms move out of the $(210)_{\text{cubic}}$ planes. Finally, the $(301)_{\text{ortho}}$ crystal planes are fully occupied by an ordered arrangement of MA cations. The complex in-plane and out of plane tilting of PbBr_6 octahedra (Table 5.1) accompanied with the increase of broken Pb-Br bonds, driving the MAPbBr_3 NCs to comminute spontaneously along $(301)_{\text{ortho}}$ crystal planes under compression. First-principles calculations are consistent with the experimental observations, where the $(210)_{\text{cubic}}/(301)_{\text{ortho}}$ crystal planes more

easily cleave under pressure compared to other low-index planes. Starting from the optimized cubic structure of MAPbBr₃, four low-index planes of (010)_{cubic}, (011)_{cubic}, (111)_{cubic}, and (210)_{cubic} were constructed using slab models¹⁵²⁻¹⁵⁴, in which a set of infinite periodic layers separated by (>15 Å) create a synthetic surface (Fig. 5.6). Each low-index plane consists of a pair symmetrically terminated slabs with four surfaces exposed to vacuum. The comminution energy of each low-index plane can be obtained as:

$$\gamma = \frac{E_{slab(A)} + E_{slab(B)} - nE_{bulk}}{4A}$$

where γ is the comminution energy; E_{slab} is the total free energy of the slabs with two complementary terminations (A and B) for each surface; n is the total surface layer number in each low-index plane and E_{bulk} is the total energy of the bulk MAPbBr₃ crystal.

Fig. 5.6 The calculated surface slab models for (010), (110) and (111) crystal planes.

In this manner, (210)_{cubic} crystal planes were constructed with stoichiometric MABr-termination and PbBr₂-termination without polarization (Fig. 5.5 (b)). The calculated cleavage energy for other three low-index surfaces: 24.7 meV/Å² for (010)_{cubic} surfaces, 20.8 meV/Å² for (110)_{cubic} surfaces, and 29.8 meV/Å² for (111)_{cubic} surfaces, which manifests with our crystal morphology in Fig. 5.1 (b). As a comparison, in the orthorhombic system at 2.5 GPa, (301)_{ortho} shows a higher cleavage energy of ~117 meV/Å², demonstrating this crystal planes more easily cleave along the (301)_{ortho} under pressure.

5.2.4 Steady-state and Time-resolved photoluminescence measurements.

Steady-state and time-resolved photoluminescence (TRPL) spectroscopy tracked the evolution of optical behaviors associated with pressure-induced morphological changes and polymorphic transitions (Fig. 5.7). Similar to the pressure optical response of MAPbBr₃ single crystal³ (Table 5.2), a red shift (from 533 to 546 nm) of the PL emission peak at < ~1 GPa in the *Pm* $\bar{3}$ *m* polymorph, is followed by a continuous blue shift in the *Im* $\bar{3}$ (from 546 to 525 nm) and *Pnma* polymorphs (from 522 to 502 nm) (the circles in Fig. 5.7 (b)). Above ~4.0 GPa, MAPbBr₃ starts to be amorphous with extremely broad and weak emission (Fig. 5.8). The band gap narrowing in *Pm* $\bar{3}$ *m* could be ascribed to Pb-Br bond length contraction (Fig. 5.3 (a)), leading to the enhancement of ~60 times in PL emission intensity^{41, 155} (the squares in Fig. 5.7 (b)). Further compression decreases the Pb-Br-Pb bond angle (Fig. 5.3 (b)) along with reduced Pb *s* and Br *p* orbital coupling^{7, 155}, resulting in band gap widening. Discontinuities in PL intensity at ~0.8 GPa and ~2 GPa arise from nonradiative recombination introduced by octahedral tilting and the onset of the

pressure-induced amorphization³ as well as the presence of surface defects during comminution.

Fig. 5.7 Structure-property correlation of MAPbBr₃ NCs during high pressure-induced comminution and recrystallization. (a) The steady-state photoluminescence (PL) and absorption measurement of NCs (0 GPa - 3.05 GPa) before amorphization. (b) The peak position and relative intensity of NCs during compression (c) Time-resolved PL (TRPL) measurement of NCs before amorphization and the mean carrier lifetime under compression. The colorful shallows represent three phases: *Pm* $\bar{3}$ *m* cubic, *Im* $\bar{3}$ cubic and *Pnma* orthorhombic phase.

Table 5.2. Comparison band gap evolution under high pressure between MAPbBr₃ single crystals and nanocrystals.

Sample	cubic <i>Pm</i> $\bar{3}$ <i>m</i>	cubic <i>Im</i> $\bar{3}$	orthorhombic <i>Pnma</i>	amorphous	Released pressure to 0 GPa
MAPbBr ₃ single crystal	0 GPa	0.4-1.1 GPa	>1.8 GPa	>3 GPa	cubic <i>Pm</i> $\bar{3}$ <i>m</i>
MAPbBr ₃ nanocrystal	0 GPa	0.6-1.47 GPa	>1.84 GPa	>3.05 GPa	cubic <i>Pm</i> $\bar{3}$ <i>m</i>

Fig. 5.8 *In situ* high pressure optical absorption and PL spectra of MAPbBr₃ NCs under compression (4.88-10.32 GPa) and release. (a, b) Absorption and PL emission are measured from 4.88 GPa to 10.32 GPa. A broad emission occurs (>4 GPa) due to pressure-induced sample amorphization. (c, d) Absorption and PL emission are measured upon decompression. After release pressure, narrow and green PL emission reverses back. A halogen lamp was used for absorption measurement as white light source. A 457 nm continuous (CW) laser was used for PL measurement.

Phase transitions and morphological changes of the NCs inevitably modifies carrier dynamics that can be analyzed through TRPL spectral fitting. A biexponential treatment ($I_{PL}(t) = I_{int} [A_{slow} \exp(-t/\tau_{slow}) + A_{fast} \exp(-t/\tau_{fast}) + I_0]$) can be used to extract the mean carrier time ($\langle \tau \rangle = [A_{slow} \tau_{slow}^2 / (A_{slow} \tau_{slow} + A_{fast} \tau_{fast})] + [A_{fast} \tau_{fast}^2 / (A_{slow} \tau_{slow} + A_{fast} \tau_{fast})]$) (Fig. 5.7 (c)), where τ_{slow} and τ_{fast} are assigned

to a bulk component and a surface component respectively^{7, 23} (see more fitting details in Fig. 5.9).

Fig. 5.9 Time-resolved photoluminescence (TRPL) measurement during compression. (a) PL decay kinetics of MAPbBr₃ NCs under pressure. (b-d) Carrier lifetime analysis using a biexponential decay function, $I_{PL}(t) = I_{int} [A_{slow} \exp(-t/\tau_{slow}) + A_{fast} \exp(-t/\tau_{fast}) + I_0]$, where $I_{PL}(t)$ is the time-dependent PL intensity; I_{int} is the initial PL intensity; I_0 is the background PL count; τ_{slow} and τ_{fast} are the fast and slow carrier lifetimes (the top panel); A_{slow} and A_{fast} are contribution of fast and slow lifetime amplitudes (the middle panel). The average lifetime $\langle \tau \rangle$ is calculated using the following relationship: $\langle \tau \rangle = [A_{slow} \tau_{slow}^2 / (A_{slow} \tau_{slow} + A_{fast} \tau_{fast})] + [A_{fast} \tau_{fast}^2 / (A_{slow} \tau_{slow} + A_{fast} \tau_{fast})]$, and is dependent on the relative contribution (A_{slow}/A_{fast} as shown in the bottom panel) between τ_{slow} and τ_{fast} .

The mean carrier lifetime is prolonged in $Pm\bar{3}m$ under mild compression due to lattice shrinkage¹⁴⁵ and surface reconstruction¹⁵⁶ with the dramatically changing of the fast and slow components (Fig. 5.9 (b,c)). Upon further compression, the larger band gap (Fig. 5.7 (b)) creates both trap states relatively deeper, leading to more nonradiative recombination⁷ and lifetime shortening. At the crucial pressure point of ~ 2 GPa lifetimes shorten to minimum $\sim 7.8 \pm 0.6$ ns due to the creation of numerous surface states introduced by comminution where the fast and slow component become comparable (Fig. 5.9 (c)). Amorphization leads to broadband emission from self-trapped states induced by a loss of periodicity, insertion of interfacial faults, and higher concentration of grain boundaries during pressure (Fig. 5.8).

Distinct from large hybrid perovskite crystals, the optical properties of MAPbBr₃ NCs cannot be restored upon decompression from ~ 11 GPa. The PL is blue-shifted ~ 5 nm with an ~ 15 -times enhancement in the emission for the large NPs (Fig. 5.10 (a)), due to strengthened quantum confinement arising from pressure-induced comminution of the NCs into nanoslices. The mean carrier lifetime shortens from $\sim 18.3 \pm 0.8$ ns to $\sim 7.6 \pm 0.5$ ns (Fig. 5.10 (b)) as more surface states exist in the perovskite NPs (Fig. 5.4 (h)). The pressure-produced highly luminescent hybrid perovskite NPs with a shorter carrier lifetime show potentially applicable to nanolasers and light-emitting diodes.

Fig. 5.10 Comparison of optical properties between the original MAPbBr₃ NCs and the pressure-synthesized MAPbBr₃ NPs. (a, b) Steady-state PL and absorption spectra and TRPL kinetics before (grey) and after (red) compression with pressure up to 11 GPa.

5.3 Conclusions

In summary, it is demonstrated to the first time that pressure can regulate the comminution and recrystallization of MAPbBr₃ NCs. The dissociation of the NCs is driven by PbBr₆ octahedral tilting and MA cation re-orientation accompanying transformation to the orthorhombic polymorph. This growth mechanism differs from that in metallic/organic semiconductor nanoparticles (Au, Ag, CdSe, PbS)^{138, 142, 143} and CsPbBr₃ perovskite QDs¹⁴⁵, *i.e.*, pressure-derived large single-crystal formation from direct attachment and sintering of those nanoparticles. New optical properties appear after a single pressure cycles, *e.g.*, the PL peak is blue-shifted ~ 5 nm with ~ 15 -time enhancement in PL emission, and the carrier lifetime halves. The application of external pressure is a simple route for engineering perovskite nanocrystals with prescribed quantum properties, and may prove useful for fabricating of micro-/nano-electronic devices.

Chapter 6 High Pressure Reponse of Crystal Structure and Excitonic Property in $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ 2D Layered Perovskite

6.1 Motivation

Compared to 3D hybrid perovskites, the 2D Ruddlesden-Popper layered hybrid halide perovskites display the improved structural stability in the humid environment, *e.g.*, at least two-month stability in air^{17, 157} and the rapid rise in photovoltaic performances with PCE up to 12.52% in the latest record^{157, 158}. Resolving the structure-property relationship of two-dimensional (2D) layered organic-inorganic hybrid perovskites is essential for their photovoltaic and photoelectronic applications as the nature-formed quantum wells, since the structural distortions correlate with the crystal stability and excitonic structure.

As discussed in section 1.4, the general structure of the 2D layered lead halide perovskites is $(\text{RNH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{M}_n\text{X}_{3n+1}$, where R is an alkyl or aromatic moiety, *e.g.*, $\text{C}_4\text{H}_9\text{NH}_3^+$ (BA) and $\text{C}_8\text{H}_9\text{NH}_3^+$ (PEA); M is a metal cation Pb_2^+ and X is a halide ion, *e.g.*, Cl^- , Br^- , I^- ; n is the number of the inorganic layers composed of in-plane corner-sharing PbX_6 octahdra and sandwiched by two long organic chains¹⁶. The pure-phase 2D layered lead halide perovskites are for n=1, only one inorganic layer sandwiched by alkylammonium layers⁷³, where electrons and holes are confined within the inorganic layers to form excitons at room temperature with binding energy up to few hundreds of meV¹⁵⁹. In addition, the direct band gap of 2D perovskites can be continuously tuned by varing the inorganic layer number n, to

cover the whole visible spectral region¹⁶⁰. These distinctive features with tunable emission and flexible structures make 2D layered lead halide perovskites also superior materials for optoelectronic applications¹⁶¹, including tunable and efficient light emitting diodes (LEDs)¹⁶², nonlinear optical switches¹⁶³, and white light-emitting devices⁷⁷.

High pressure up to gigapascal, offers a comprehensive way to study the structure-property correlation of solid materials in the atomic level, where both crystal structures and electronic properties are changed dramatically¹⁶⁴. Numerous high pressure work has been done for 3D lead halide perovskites, for example, high pressure-induced phase transformations, amorphization, electronic transitions, increased conductivity, carrier-lifetime prolongations^{7, 42, 129, 159, 165-167}. More recently, two high-pressure studies of Cu-Cl layered hybrid perovskites are reported, demonstrating the high-pressure induced shrinkage and distortion of CuCl_4^{2-} coordinates along with band gap narrowing^{80, 168}. However, these Cu-based layered perovskites with strong electron-phonon coupling limit their photovoltaic and optoelectronic applications¹⁶⁹ as compared to the 2D layered lead halide perovskite materials. Under these considerations, we choose the BAPI 2D perovskite, *i.e.*, BAPI, for high-pressure studies. Preliminary high-pressure work only shows the red-shifted absorption and photoluminescence spectra of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ ¹⁷⁰ and $(\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{PbI}_4$ ¹⁷¹ perovskites without any deep physical analysis of the pressure effects on the structural and electronic/excitonic properties.

In this study, a thorough high-pressure study of the BAPI 2D layered perovskite with $n=1$ is reported for the first time, where three structural symmetries under high

pressure before amorphization are resolved by retrieving the structural parameters from the *in situ* XRD patterns, *i.e.*, *Pbca* (*1b*) RT phase, *Pbca* (*1a*) LT phase and *P2₁/c* HP phase. Abnormal pressure responses of excitons are investigated, where a blue jump followed by a monochromic red shift in photoluminescence (PL) spectra, and a dual emission in certain pressure range is observed for the first time in 2D layered perovskites. Such exciton behaviors closely correlate with structural evolutions upon compression, and the mixed-phase coexistence is the origin of the dual emission. Besides, exciton shows distinct dynamic properties in different phases. Therefore, a comprehensive study on structural evolutions and functional property variations in extreme case, *i.e.*, high pressure, would be helpful for real utilization of 2D layered perovskite materials.

6.2 Results and discussions

6.2.1 High pressure response of the crystal structures.

The exfoliated flake of BAPI solution-grown single crystals is transferred onto the surface of the DAC and is protected by BN layer (section 3.3), the schematic DAC and optical image of the sample as shown in Fig. 6.1 (a,b). The sample area tracked for the high pressure experiment is marked by the blue star with thickness ~50 nm, which is estimated according to the relationship between the thickness and optical contrast (Fig. 6.2). The as-grown yellow microcrystals perform strong one excitonic absorption and emission peak (Fig. 6.3 (a)), demonstrating a good pure-phase (n=1) 2D layered perovskite. Under ambient conditions, BAPI crystallizes in orthorhombic space group *Pbca* (*1b*), *i.e.*, room-temperature (RT) phase. The lattice parameter is $a=8.85\text{\AA}$, $b=8.66\text{\AA}$ and $c=27.60\text{\AA}$ from the refinement of the XRD pattern measured at 0 GPa as shown in Fig. 6.3 (b)¹⁷². Fig. 6.1 (c) shows the

corresponding two-dimensional arrangement of BAPI, where the inorganic PbI_6 sheets are separated by two organic layers of mutually interdigitated BA cations, and the adjacent inorganic is in staggered arrangement due to the tilted PbI_6 octahera induced by hydrogen-bonding interaction¹⁷³ between the NH_3^+ groups and the I ions (the inset in Fig. 6.1 (c)). Upon compression, BAPI displays a series of piezochromic transition (Fig. 6.1 (d)), from yellow to translucent yellow to translucent brown to translucent red and ended by black color. Fig. 6.1 (e) shows the corresponding absorption spectra from the extremely strong excitonic transitions are shown in where the evolution between absorption peak I and peak II, demonstrates clear structural phase transitions and two-phase coexistence¹⁷⁴.

Fig. 6.1 BAPI (BA = $\text{C}_4\text{H}_9\text{NH}_3^+$) 2D layered perovskite single crystal under compression. (a-c) The optical image of exfoliated flake on the diamond surface of the symmetric DACs; schematic crystal structure of orthorhombic *RT*-BAPI. (Inset) BA organic chain. (d-e) Optical micrographs of piezochromism and the corresponding absorption spectra under selected pressures.

Fig. 6.2 Thickness determination of BAPI single crystals. (a) Optical images of mechanical exfoliated BAPI 2D perovskite. The light blue flakes are around 6 nm thick, consisting of 3-4 layers of unit cell. Scale bar is 10 μm. (b) Optical images of h-BN fully encapsulated BAPI flakes. Scale bar is 10 μm. (c) AFM height image of h-BN encapsulated BAPI. The h-BN and BAPI Thicknesses are determined to be 6 and 8 nm, respectively. Inset is the height profile along the section indicated by the vertical white line. AFM measurements are performed for the transferred sample onto the silicon substrate. Once the relationship between the thickness and optical contrast is established, the thickness can be estimated according to the optical contrast without measuring the actual thickness¹².

Fig. 6.3 Characterization of BAPI single crystals. (a) Absorption and PL spectra measured at ambient condition. (b) Refinement of the 0 GPa XRD data with orthorhombic space group *Pbca* (1b).

To resolve the optical property-structure correlation of BAPI crystal under high pressure, we performed the *insitu* synchrotron powder XRD with pressure up to 7.6 GPa and release, the representative integrated XRD spectra as shown in Fig. 6.4 (a). The first structural transition occurs at extremely low pressure ~ 0.32 GPa, along with apparent peak broadening and abruptly discontinuous shifting as compared to the initial pattern (RT phase). The Reitveld refinement profile at ~ 1.15 GPa demonstrates the BAPI sample is in the orthorhombic space group $Pbca$ ($1a$), *i.e.*, low-temperature (LT) phase (Fig.6.5 (a)). Another new set of diffraction patterns appear at high pressure ~ 5 GPa, accompanying with two new peaks at $2\theta = 4.77^\circ$ and 4.97° , respectively. We assign the BAPI sample beyond 5 GPa is in the monoclinic space group $P2_1/c$, *i.e.*, the high-pressure (HP) phase (Fig.6.5 (b)). The structure evolution from LT phase to HP phase across over a broad pressure range of ~ 4 GPa, *i.e.*, from ~ 1 GPa to 5 GPa, where the peak intensity of HP-BAPI becomes stronger and stronger and all peaks do not broaden obviously, demonstrating the mixed phase nature¹⁶⁸. It is obvious that there is a high-energy hindrance¹⁷⁵ between LT and HP phases, indicating high pressure technique is an effective way to drastically tune crystal structures.

Fig. 6.4 Structural evolution under high pressure. (a) Integrated synchrotron XRD profiles under compression and release to ambient pressure. (b-c) Organic-inorganic packing diagrams and the orientation of BA chains in three phases. The dashed back lines represent the parallelogram formed by adjacent bridging I atoms. The red dotted lines represent the hydrogen-bonding.

Fig. 6.5 Rietveld refinement of BAPI under representative pressures. (a) Refinement of the 1.15 GPa XRD data with orthorhombic space group $Pbca$ ($1a$); (b) Refinement of the 5.18 GPa XRD data with monoclinic space group $P2_1/c$. Simulation results in red.

Compared to the RT phase, an in-plane (a-b plane) rotation of neighboring PbI_6 octahedra, the crystal structural transition into LT phase is determined by the additional out-of-plane tilting (the atomic structures as displayed in Fig. 6.4 (b)) and the reorientation of organic chains (the top view projection in Fig. 6.4 (c))¹⁷², where the butylammonium molecule is orientated almost parallel to the short diagonal in the LT phase instead of the long diagonal of the parallelogram (four bridging I2 atoms) in the RT phase. In RT phase, the BA molecule is orientated along the long diagonal of the parallelogram formed by adjacent bridging I atoms, where the two H atoms of the NH_3^+ end are formed hydrogen-bonding with two terminal I atoms (I1) and one H atom is formed hydrogen-bonding with the bridging I atom (I2). Upon compression, the BA molecule moves relative to the parallelogram away from an acute angle to an obtuse angle and is almost orientated along the short diagonal. One H atom of NH_3^+ chooses a different terminal I atom to form hydrogen-bonding, leading to a distinct tilting of PbI_6 octahedra and triggering a structural phase transition from RT ($Pbca$ ($1b$)) phase to LT ($Pbca$ ($1a$)) phase. The distinct hydrogen-bonding interaction between the ammonium group and I ions leads to the much more tilting of PbI_6 octahedra and larger offset of inorganic layers¹⁶⁸ in LT phase (Fig. 6.4 (b)). In contrast to the RT-LT phase transition, the pure HP structural transition involves a movement in half unit cell along a direction of the adjacent inorganic layers in LT phase (the HP structural model in Fig. 6.4 (b)) as well as the deviation of the butylammonium molecule relative to the short diagonal of the parallelogram¹⁷² (Fig. 6.4 (c)).

6.2.2 High pressure response of the excitonic structures.

The PbI_6 octahedra tilting definitely influences the excitonic structure of BAPI to further effect the optical properties, as presented by the *insitu* photoluminescence (PL) spectra under pressure in Fig. 6.6 (a). The PL envolution is similar to the absorption (Fig. 6.1 (e)), indicating these two peaks are from intrinsic exciton recombination instead of defects emission. Initially, the emission peak I suddenly blue jumps ~ 18 nm at ~ 0.33 GPa, manifesting the RT-LT phase transition for the temperature-dependent PL results (Fig. 6.7), and keeps consecutive red shift up to ~ 1.2 GPa. Further increasing pressure, along with the HP structure growing up (Fig. 6.4 (a)), additional emission peak II is observed, which is from the luminescent emission of the coexisting HP phase^{107, 176}. At ~ 2 GPa, the PL emission profile has changed obviously along with the more intense peak II of HP phase, instead the peak I of LT phase gradually becomes weaker and weaker. Up to ~ 3 GPa, the emission peak I of LT phase has disappeared totally, and the emission peak II of HP has become dominant and keeps red shift before amorphization (~ 7.6 GPa), where a broad emission profile of polaron is observed (Fig. 6.8 (a,b))¹⁷⁷.

The excitonic structural evolution of BAPI under compression, the high-pressure *in situ* PL spectra are measured (Fig. 6.6 (a)). To explore the correlation between the excitonic structure and PbI_6 coordination, we plot the band gap (via fitting the PL spectra) as a function of pressure, the spheres as shown in Fig. 6 6 (b). The calculated results (the hollow dots) match well with our experimental results, where the band gap red shifts more obviously in HP phase as compared to that in LT phase. The calculated results based on a series of crystal structures exhibit an consistent trend

of bandgap evolution with the experimental observation, revealing that the high-pressure-induced structural distortions control the variation of bandgap.

As discussed in sub section 1.4.2, the conduction band minimum (CBM) of organolead halid perovskites is formed by antibonding couplings of the Pb $6p$ and I $5s/5p$ hybrid orbitals, while the valence band maximum (VBM) is determined by the antibonding interactions of the Pb $6s$ and the I $5p_x/5p_y$ orbitals, as shown in Fig. 6.6 (c). According to the calculated structures, the PbI_6 octahedra tilt a lot upon compression, where the much more bended bridging angle $\langle \text{Pb-I-Pb} \rangle$ results in a loss of the Pb-I orbital overlap and weakens antibonding interactions of the Pb $6s$ orbital and the I $5p_x/5p_y$ orbitals, thus pulling down the top of valence band. Instead, the bottom of conduction band will be pushed up still due to weakened couplings of Pb $6p$ and the I $5s/p$ hybrid orbitals. As a conclusion, the bending in $\langle \text{Pb-I-Pb} \rangle$ bridging angle leads to a widening (blue shift) in the band gap (the blue ink long box in Fig. 6.6 (c)). In addition, the shortening of equatorial Pb-I bond lengths upon compression enhances Pb-I antibonding interactions to lower the CBM and lift the VBM, leading to a narrowing (red shift) in the band gap (the red long box in Fig. 6.6 (c)). Thus, we extract these two important parameters from the calculated structures and plot the bond angle (Fig. 6.6 (d)) and the bond length (Fig. 6.6 (e)) as a function of pressure, to systematically elucidate the physical mechanism behind the structure-property correlation under pressure. The considerably bended $\langle \text{Pb-I-Pb} \rangle$ bond angle and the elongated two equatorial Pb-I bond lengths all contribute to the blue jump in the measured PL spectrum at the RT-LT phase transition pressure point of 0.33 GPa^{3, 7, 155}. On the other hand, in the $P2_1/c$ HP structure, the $\langle \text{Pb-I-Pb} \rangle$ bond angle is almost restored back to 0 GPa and further increases with pressure, while the two equatorial Pb-I bond lengths still become shorter, all contributing to a narrowing in

bandgap⁷. and a more pronounced red shift in HP phase compare to LT phase. It is clear that the high-pressure-induce variation in the band gap is a joint action of the $\langle \text{Pb-I-Pb} \rangle$ bond angle and Pb-I bond length. At phase transition point, the Pb-I-Pb bond angle is a dominant structural factor impacting the band gap, while equatorial Pb-I bond length is a secondary influence on the excitonic structure in each phase.

Fig. 6.6 Correlation of structure-optical property of BAPI single crystal under high pressure. (a) Pressure-driven blue jump/red shift and due-emission in static PL spectra. (b) The conduction band maximum (CBM) and valence band minimum (VBM) of BAPI associated with the interaction between Pb and I orbitals as shown in the isosurfaces of electron density. (c) Exciton evolution as a function of pressure: experiment (blue ink spheres) and calculation (violet hollow dots), respectively. The colorful shallows represent phase evolution with increasing pressure. (d-e) The evolution of $\langle \text{Pb-I-Pb} \rangle$ bridging angle α (orange symbols) and two equatorial Pb-I bond lengths (pink and cyan symbols) as the function of pressure.

Fig. 6.7 The temperature-dependent PL spectra. PL peak blue jumps ~20 nm during RT-LT phase transition temperature ~250 K.

Fig. 6.8 High pressure-induced polaron emission. (a-b) Absorption and PL spectra at 0 GPa (grey) and 10 GPa (violet).

6.2.3 High pressure response of the carrier dynamics.

High pressure-induced significant changes in excitonic structure of BAPI single crystal may provide different relaxation pathways for excitons to further influence the carrier properties. Thus, high-pressure time-resolved photoluminescence (TRPL)

measurements are implemented for the first time in hybrid 2D layered perovskite single crystals, the results at representative pressures are illustrated in Fig. 6.9 (a-d). At ambient pressure (RT phase), the mean exciton lifetime is $\sim 144.8 \pm 18.0$ ps, where the fast decay channel of free excitons is $\sim 50.9 \pm 1.0$ ps and the slow decay channel of trapped excitons is $\sim 324.9 \pm 11.7$ ps, consistent with previous reported timescale for n=1 BAPI thin single crystals^{161, 178}, the corresponding simplified (trap states not presented) decay channel 1 shown in Fig. 6.9 (e). Longer exciton lifetime of $\sim 187.7 \pm 11.3$ ps is observed in 0.39 GPa LT phase, due to more trap states introduced by pressure-induced lattice distortion of inorganic PbI_4^{2-} layer^{7, 166, 167}, the corresponding simplified decay channel 1 (with more trap states) shown in Fig. 6.9 (e). Further increasing pressure up to 2.3 GPa, *i.e.*, LT and HP mixed phase, an exciton lifetime of $\sim 52.8 \pm 6.6$ ps is observed, such significant shortening can be ascribed to the carrier funnelling process^{15, 160} from higher excitonic states of LT phase to lower excitonic states of HP phase, involving simple decay channel 1 and complex decay channel 3 with interband transition (black arrow) as illustrated in Fig. 6.9 (e). In the high-pressure (3.6 GPa) pure HP phase, the exciton decay is single channel (decay channel 3 in Fig. 6.9 (e)) with lifetime of $\sim 35.8 \pm 5.1$ ps.

Fig. 6.9 Carrier lifetime in different phases. (a-d) TRPL spectra of BAPI single crystal at 0 GPa (RT phase), 0.39 GPa (LT phase), 2.3 GPa (LT and HP mixed phase) and 3.6 GPa (HP phase). All the TRPL spectra were obtained from the peak I in static PL spectra. A biexponential treatment ($I_{PL}(t) = I_{int} [A_{slow} \exp(-t/\tau_{slow}) + A_{fast} \exp(-t/\tau_{fast}) + I_0]$) used to extract the mean carrier time ($\langle\tau\rangle = [A_{slow} \tau_{slow}^2 / (A_{slow} \tau_{slow} + A_{fast} \tau_{fast})] + [A_{fast} \tau_{fast}^2 / (A_{slow} \tau_{slow} + A_{fast} \tau_{fast})]$), where τ_{slow} and τ_{fast} are assigned to the trapped and free exciton recombination respectively. (e) The correlation between carrier lifetime and decay channel in different phases.

6.3 Conclusions

We have investigated experimentally the pressure-induced phase transitions in BAPI 2D layered perovskite with $n=1$, where detailed structural information is resolved for the first time, including variations of inorganic PbI_4^{2-} layers and reorientations of organic BA molecules during $Pbca(1b) \rightarrow Pbca(1a) \rightarrow P2_1/c$ phase transitions. Meanwhile, we realized the excitonic bandgap narrowing and dual emission in the high-pressure condition, associated with inorganic lattice distortions and the mixed-phase ($Pbca(1a)$ and $P2_1/c$) coexisting. Furthermore, exciton lifetime is demonstrated strong dependence on the structural properties. High pressure, as an effective tool, can tune lattice structure in a precise and controllable way, further to

realized better materials with improved performances. Therefore, high-pressure explorations on 2D hybrid lead halide perovskites provide us deeper insight into the structure-property correlation from the atomic point of view, which is crucial for their further photovoltaic and photoelectric applications with optimized crystal structures and functional properties.

Chapter 7 Future Work

We have comprehensively studied the optical properties of hybrid perovskites from 3D to 2D and nanocrystals under high pressure and low temperature, where the Raman, absorption, photoluminescence and carrier lifetime were implemented. By combining the powder XRD, TEM and *ab initio* calculations, we obtained the following research results so far:

1. Identify the dynamics of the MA orientations and the hydrogen-bonding in MAPbBr₃ during temperature-dependent polymorphic transformation. The key outcome is that H_C $\cdots$ Br becomes significant only in the low temperature orthorhombic polymorph, which rationalizes the state of the MA cations and the concomitant tilting of PbBr₆ octahedra with the consequent dynamical change of the band structures, *i.e.*, indirect bandgap to direct bandgap transition. Developing a quantitative understanding of the strength and orientation of the hydrogen-bonding of the MA cations is the first step towards optimizing the optoelectronic properties of this class of materials for solar cell and related applications.
2. Demonstrate for the first time that pressure can regulate the comminution and recrystallization of MAPbBr₃ NCs. The dissociation of the NCs is driven by PbBr₆ octahedral tilting and MA cation re-orientation accompanying transformation to the orthorhombic polymorph. New optical properties appear after a single pressure cycles, *e.g.*, the PL peak is blue-shifted ~ 5 nm with ~ 15 -time enhancement in PL emission, and the carrier lifetime halves. The application of external pressure is a simple route for engineering perovskite

nanocrystals with prescribed quantum properties, and may prove useful for fabricating of micro-/nano-electronic devices.

3. Detailed structural information under high pressure is resolved for the first time in BAPI 2D layered perovskite with $n=1$, including variations of inorganic PbI_4^{2-} layers and reorientations of organic BA molecules during $Pbca (1b) \rightarrow Pbca (1a) \rightarrow P2_1/c$ phase transitions. Meanwhile, excitonic bandgap narrowing and dual emission are realized via high-pressure treatment, associated with inorganic lattice distortions and the mixed-phase ($Pbca (1a)$ and $P2_1/c$) coexisting. Furthermore, exciton lifetime is demonstrated strong dependence on the structural properties. High-pressure explorations on 2D hybrid lead halide perovskites provide deeper insight into the structure-property correlation from the atomic point of view, which is crucial for their further photovoltaic and photoelectric applications with optimized crystal structures and functional properties.

Based on our current research work, there are still many other interesting research areas should be investigated to achieve new breakthroughs in perovskite material science and to further develop application prospects of hybrid perovskite in the future.

7.1 High pressure studies on hybrid perovskites with different compounds and dimensions

7.1.1 The high-pressure studies on 3D perovskites with chemical formula ABX_3 (A=MA/FA, B=Pb/Sn, X=Cl/Br/I)

According to our current results on MAPbBr₃ 3D hybrid perovskite, where the crystal and electronic structure is changed significantly under compression. For the hybrid perovskite family, such a particular material structure can be tuned easily by replacing the compounds, such as organic group (MA⁺ or FA⁺), the metal ion (Pb²⁺ or Sn²⁺), the halide ion (Cl⁻, Br⁻, or I⁻), further to alter geometric parameter, *i.e.*, the tolerance factor (Fig. 1.1 (c)), where the tolerance factor t is used to describe the distortion of perovskite structure, the relationship as shown in Fig. 7.1 (a). The different perovskite compounds will form different crystal structures with different space groups in the ambient condition, which will behave different pressure responds¹⁴, *i.e.*, phase transition sequences, as shown in Fig. 7.1 (b-c). Based on the environmentally friendly requirement in the hybrid perovskites for the next generation photovoltaics and solar cell applications, Sn is a good candidate to replace the toxic Pb. It is important for us to comprehensively understand such a crystal structure-property correlation, including the electronic, carrier lifetime and conducting properties, in the Sn-based hybrid perovskites.

Fig. 7.1 (a) The relationship between the perovskite structure and the tolerance factor¹³. (b-c) Different structural phase transition sequences of MAPbI₃, MAPbBr₃ and MAPbCl₃ perovskites under high pressure¹⁴.

Herein, we try to apply the pressure on other hybrid perovskites, such as MA/FASn_yPb_{1-y}X₃ or MA_yFA_{1-y}SnX₃^{179, 180} not just the most popular 3D perovskites (MAPbCl₃/Br₃/I₃), to explore the evolution of optical (electronic structures carrier lifetime) and conducting properties in the lead-free or double hybrid 3D perovskites under high pressure. Previous reported work on MA_yFA_{1-y}SnI₃ perovskites only focused on pressure-induced structural changes by using synchrotron X-ray powder diffraction, *i.e.*, the phase transitions¹⁸⁰. Recently, only one work reports the improvement in the electrical conductivity of MASnI₃ lead-free perovskite after pressure treatment¹⁸¹. The pressure response from these Sn-based hybrid perovskites would provide us a new insight into crystal structures for further fabrication and utility in environmentally friendly photovoltaic and optoelectronic devices^{182, 183}.

7.1.2 The high-pressure studies on 2D perovskite with different layer numbers (n=2, 3 ...)

As discussed in sub section 1.4.2, this series quasi-2D layered perovskites, (C₄H₉NH₃)₂(CH₃NH₃)_{n-1}Pb_nI_{3n+1} with n = 1, 2, 3..., are mixed organic, multiple inorganic layered structure, bridging pure 2D (n=1) perovskites and 3D (n=∞) perovskites (Fig. 7.2 (a))¹⁶, and showing semiconducting to metallic evolution. Not only the band gap and carrier dynamics (Fig. 7.2 (b,c))¹⁵ will change with increasing the inorganic layer number, but also the structural stability will be altered (Fig. 7.2 (d-f))¹⁶.

Fig. 7.2 (a-c) The layer-dependent absorption/photoluminescence and carrier lifetime of MA-PEA 2D perovskites¹⁵. (d-f) Structural stability as a function of dimensionality¹⁶.

According to our current results on $n=1$ $(C_4H_9NH_3)_2PbI_4$ 2D perovskite, where the excitonic structure is changed significantly under compression, we will try to apply pressure on $(C_4H_9NH_3)_2(CH_3NH_3)Pb_2I_7$ $n=2$, $(C_4H_9NH_3)_2(CH_3NH_3)_2Pb_3I_{10}$ $n=3$ and $(C_4H_9NH_3)_2(CH_3NH_3)_3Pb_4I_{13}$ $n=4$ members to study the role of inorganic layer number in high pressure response of quasi-2D perovskites.

7.1.3 The high-pressure studies on 0 D perovskite with chemical formula $A_3B_2X_9$ ($A=Cs$, $B=Sb/Bi/Cr$, $X=Cl/Br/I$)

Perovskite materials with the general formula $A_3B_2X_9$ ($A=Cs/Rb$, $B=Sb/Bi/Cr$, $X=Cl/Br/I$)¹⁸⁴ have recently become hot for replacing the toxic lead element and good stability in air, another promising candidate for use in high-band gap photovoltaic devices. These compounds can form a dimer 0D structure with hexagonal space group or a layered 2D structure with trigonal group space according to certain growth conditions¹⁷. However, structural evolution and properties in this kind of perovskites only has been widely studied in low temperature condition, where a few phase transitions were found below extremely low temperature ($< 90K$)

by nuclear magnetic resonance (NMR) techniques, far from a complete phase transition picture¹⁸⁵. And another X-ray study of Cs₃Sb₂I₉ trigonal crystal demonstrated three phase transitions at 86K, 78K and 72K, and an intermediate incommensurate phase was detected between 78-72K¹⁸⁶.

High pressure (up to tens of gigapascal), as a clean, simple and quick technique, can drastically change the material structures and physical/chemical properties. Herein, we will apply hydrostatic pressure on one of this class of perovskites, Cs₃Sb₂I₉ single crystal, to explore the structural phase transition of 2D layered and 0D dimer crystals (Fig. 7.3 (a, b)). The 2D layered Cs₃Sb₂I₉ polymorph possesses $P\bar{3}m1$ trigonal group space, the SbI₆ octahedra are corner-sharing (Fig. 7.3 (a)). While the 0D dimer Cs₃Sb₂I₉ polymorph possesses $P6_3/mmc$ hexagonal group space, the pairs of SbI₆ octahedra share faces (Fig. 7.3 (b)). Such structural feature of Cs₃Sb₂I₉ crystals, *i.e.*, different stacking of SbI₆ octahedra layers and weak bonding to each other, shows easy cleavage properties along the layers¹⁸⁵. Another interesting distinction between these two structures is the electronic structure, the calculated band structure for the layered and dimer polymorphs are shown in Fig. 7.3 (c, d). The layered structure is direct band gap nature with a gap energy of ~2.05 eV, while a larger indirect band gap of 2.40 eV is calculated for the dimer structure. As speculated, the electronic responses under compression would be different based on distinct pressure-induced structural evolution in these two polymorphs, and it is inspired that if the indirect to direct band gap transition could be realized under certain pressure.

Fig. 7.3 (a-b) The perovskite structure in the 2D layered modification and dimer modification of $\text{Cs}_3\text{Sb}_2\text{I}_9$. Cs atoms (orange spheres), I atoms (green spheres) and Sb coordination polyhedra are blue. (c-d) The calculated electronic structures of two distinct structures¹⁷.

7.2 High pressure experiments of hybrid perovskites at low temperature

Organic-inorganic hybrid perovskites, as the low-cost, high-efficiency light absorbers, exhibit potential applications in photovoltaic devices²² and solar cells¹⁶⁸. Therefore, it is important to not only fully understand the structural stabilities and optoelectronic properties of perovskite materials but also to realize new features. Pressure can drastically change the structures and physicochemical properties in solids, and most of physical phenomena can only be clearly studied at low

temperatures¹⁸⁷. However, the recent numerous reported phase transitions in hybrid perovskites either under high pressure at room temperature or upon cooling in ambient pressure, which is far from the real research requirements. Most of condensed matters undergo distinct phase transition sequences under high pressure¹⁴ or at low temperature⁴⁹, as demonstrated by the P-T phase diagram of BaTiO₃ in Fig. 7.4. To fill this research gap in the P-T phase diagram of hybrid perovskites, the structural evolution must be explored under certain scale of pressure and over a broad range of temperature, or at certain temperature and various pressures¹⁸⁸.

Fig. 7.4 The P-T phase diagram for BaTiO₃ combined with the low-temperature data and classical extrapolation¹⁸.

Herein, we will apply the high pressure on MAPbBr₃ perovskite single crystal at low temperatures to plot a complete P-T phase diagram for this material. MAPbBr₃ perovskite undergoes phase transition sequence under high pressure: $Pm\bar{3}m$ cubic - $Im\bar{3}$ cubic - $Pnma$ orthorhombic phase and also performs three phase transitions upon cooling: $Pm\bar{3}m$ cubic - $I4/mcm$ tetragonal - $Pnma$ orthorhombic phase, which is a good candidate for high pressure combined with low temperature studies. Our

results will provide a new insight into hybrid perovskites for further engineering and fabricating perovskite materials with high qualities and improved functionalities.

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