Effects of organic cations on optical properties and structural stability in two-dimensional hybrid perovskites

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**EFFECTS OF ORGANIC CATIONS ON OPTICAL
PROPERTIES AND STRUCTURAL STABILITY IN TWO-
DIMENSIONAL HYBRID PEROVSKITES**

YULIA LEKINA

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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DIMENSIONAL HYBRID PEROVSKITES**

YULIA LEKINA

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2021

Statement of Originality

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

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Prof Ze Xiang Shen

Authorship Attribution Statement

This thesis contains material from 1 paper(s) published in the following peer-reviewed journal in which I am listed as an author.

Chapter 3 is published as Lekina, Y. & Shen, Z. X. Excitonic states and structural stability in two-dimensional hybrid organic-inorganic perovskites. *J. Sci. Adv. Mater. Devices* **4**, 189–200 (2019), DOI: 10.1016/j.jsamd.2019.03.005.

The contributions of the co-authors are as follows:

- Prof Shen supervised the project and edited the manuscript drafts.
- I found and reviewed the papers and prepared the manuscript drafts.

Besides, this thesis contains material from 2 papers submitted or to be submitted in the following peer-reviewed journals in which I am listed as an author.

Chapter 4 is submitted as Yulia Lekina, Sai S.H. Dintakurti, Jiaxu Yan, Benny Febriansyah, Jason England, Tim White, John Hanna, Ze Xiang Shen*. Organic Cations Dynamics and Optical properties in (PEA)₂(MA)[Pb₂I₇] Perovskite Dimorphs

The contributions of the co-authors are as follows:

- Prof Shen supervised the entire work, participated in the discussion, and edited the manuscript drafts.
- Prof England provided the materials and edited the manuscript draft.
- Prof Tim White participated the discussion about the structure of the material, and he edited the manuscript draft.
- Prof Hanna interpreted and discussed the Nuclear Magnetic Resonance, and he edited the manuscript draft.
- I prepared the manuscript drafts. Mr Dintakurti and Prof Hanna contributed the chapter about Nuclear Magnetic Resonance.

- I designed and performed all optical spectroscopic experiments: photoluminescence, optical absorption, Raman, including temperature-dependent. I also analyzed and discussed the results.
- Dr. Febriansyah performed the materials synthesis.
- Mr. Dintakurti performed the collected X-ray diffraction pattern and performed differential scanning calorimetry of the sample. He also conducted and analyzed solid-state Nuclear Magnetic Resonance spectra.
- Dr. Yan conducted first principles calculations.

Chapter 5 is submitted as Yulia Lekina, Benny Febriansyan, Xiaofeng Fan, Lu You, Samuel Morris, Jiaxu Yan, Wang Junling, Jason England and Ze Xiang Shen. Strong Optical, Electrical and Raman in-Plane Anisotropy in Corrugated Two-Dimensional Perovskite. The paper is currently under review in *Nature Communications*.

The contributions of the co-authors are as follows:

- Prof Shen supervised the entire work, participated the discussion, and edited the manuscript drafts.
- Prof England provided the materials and edited the manuscript draft.
- I prepared the manuscript drafts.
- I designed and performed all optical experiments: photoluminescence, optical absorption, reflectivity, Raman, including temperature-dependent. I also analyzed and discussed the results.
- Dr. Febriansyan performed the materials synthesis
- Dr. Lu You designed and perform electrical experiments.
- Dr. Morris performed structural characterization: he collected and refined single crystal, determined the crystallographic directions in the crystals.
- Dr. Fan conducted first principles calculations, including the band structure and dielectric constant calculations. He also performed simulations of the vibrations.
- Dr. Yan conducted first principles calculations, including simulations of the excitons.

Chapter 6 **does not** contain any materials from papers published in peer-reviewed journals or from papers accepted at conferences in which I am listed as an author.

The contributions in the project are:

- Prof Shen supervised the entire work, participated the discussion, and edited the drafts.
- I prepared the all chapter text and figures.
- I designed and performed all optical experiments: photoluminescence, optical absorption, Raman, including high-pressure study. I also analyzed and discussed the results.
- Prof Han Sen Soo and his group members provided the sample and participated the discussions.

21-Jan-2021

Date

Yulia Lekina

Abstract

Two-dimensional (2D) hybrid organic-inorganic lead halide perovskites have been extensively studied in the last few years. Tunability and improved stability over their 3D counterparts make them promising materials for applications in various technologically important areas. Extended chemical engineering possibilities allow control of the functional properties, such as band gap, light emission, conductivity or spin-related effects. 2D perovskites, consisting of alternate semiconducting inorganic lead halide and insulating organic layers, form natural multiple quantum well structures, where the optoelectronic properties are primarily determined by the inorganic sublattice, and the tunability can be directly achieved by varying the composition, thickness and structure of the lead halide layers. However, the organic layers also influence the material properties as well, for example affecting the crystal structure by sterical factors, as well as through direct interactions with the inorganic sublattice.

In this thesis, we investigate how the properties of 2D perovskites are dependent on the nature of the organic cations by utilizing optical and vibrational spectroscopy in a wide temperature and pressure range. Our work reveals that various modifications of the organic groups cause some specific changes in the perovskites. For example, combining small methylammonium MA^+ and bulky phenylethylammonium PEA^+ organic cations results in the multidimensional perovskite $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ that is significantly more stable in comparison with the 3D (three-dimensional) counterpart. On the other hand, the small MA^+ cation has rotational degree of freedom, that is not typical for the long interlayer chains. The state of the small cation is shown to influence the optical properties of the multidimensional perovskites. When a 2D perovskite with corrugated inorganic layers is formed with a relatively short asymmetric imidazolium-ethylammonium bication, strong in-plane anisotropy of the optoelectronic properties and exciton-phonon coupling were observed. The compressibility and high-pressure evolution in 2D perovskites with naturally anisotropic mechanical properties are of particular interest. Unlike other materials, PL intensity in some perovskites increase markedly under pressure. Besides, the perovskites are known to show a series of phase

transitions, which involve the Pb-I bond length and angle changes and impact the energy band gap. In 2D perovskites, the choice of the interlayer organic cation affects the phase transitions variety and structural stability. Therefore, relatively strong π - π interactions between benzene rings result in more stable and rigid perovskites. In contrast, choosing the long flexible hexadecylammonium organic cation resulted in a rich variety of responses of the material to high pressure. The thick and soft organic layer is shown to be more compressible and exhibit more degrees of freedom in response to pressure, resulting in the disordering of the organic sublattice, which in turn influence the structure of the inorganic octahedra and hence the electronic structure and optical properties.

In summary, we systematically investigated how the choice of the organic cations in 2D perovskites affects their structural and optical properties, which often results in special and exclusive features. Our work contributes to the understanding of fundamental optical and physical properties of two-dimensional perovskites.

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Chapter 1

Introduction

Since the first mineral with the perovskite structure CaTiO_3 was discovered in 1839¹, various materials repeating this crystal motif, perovskite-like materials, have been discovered. These compounds have demonstrated various functional properties such as ferroelectricity¹, optical nonlinearity², semiconductivity³, colossal magnetoresistance⁴, and multiferroic features⁵.

Traditionally inorganic materials (mostly oxides) are known to have perovskite-like structure, but recently hybrid organic-inorganic and all inorganic³ halides have attracted intense attention due to their high performance and low cost in solar cells applications^{3,6,7}. Moreover, this class of materials has been shown to be promising to use in light emitting diodes^{6,8,9}, X-ray- and photo-detectors^{10,11}, spintronics¹², batteries¹³, and lasing¹⁴. Development of the solar cell performance of hybrid halide perovskites with the general formula AMX_3 (A is an organic cation, usually $\text{MA} = \text{CH}_3\text{-NH}_3^+$ or $\text{FA} = \text{NH}_2\text{-CH}_2\text{-NH}_2^+$; $M = \text{Pb, Sn}$; $X = \text{I, Br, Cl}$ or a mixture of them) is much faster than that of other photovoltaic materials^{6,15}. Moreover, altering the composition allows tuning the band gap and optical properties of the material efficiently¹⁵.

However, poor moisture and illumination stability of regular three-dimensional (3D) hybrid organic-inorganic perovskites still remains the main obstacle to fabricate the low-cost and long-running devices^{6,12}. Two-dimensional (2D) perovskites, demonstrating better stability and extended chemical engineering possibilities, can be the next generation of materials for solar light-harvesting applications¹⁶, as well as for light emitting diodes (LEDs)^{12,17–22}.

2D perovskites represent a particular class of low-dimensional perovskites, that can be obtained from the parent perovskite structure by slicing it along one of the crystallographic planes and inserting a long organic cation in between, yielding a layered structure with corner-sharing octahedral inorganic quantum wells separated by an organic barrier. In practice it is achieved by substitution of a small cation at the A position of AMX_3 by a bulk amine R^+ . If only a part of A is substituted, so-called multilayered perovskites can be obtained^{23,24}. The generic chemical formula of the

multilayered perovskites with corner-sharing octahedra is $R_2(A)_{n-1}M_nX_{3n+1}$ (if R is a monobasic amine), where n represents the number of octahedral layers within one inorganic sheet (Figure 1)²⁵. Higher members of $R_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n > 2$) have attracted a lot of attention recently due to high efficiency at solar cell application^{17,26–29}. The $n = 5$ member demonstrated an efficiency up to 18%^{28,30,31} while the heterostructured 3D-2D perovskites exhibit PCEs up to 22%^{30,32}. Such materials have been found to be perfect materials for light emitting diodes (LEDs) due to tunability, high quantum efficiencies, and broadband emission^{12,17–21,32}.

Figure 1.1. Schematic representation of multilayered perovskites on the example of $\text{PEA}_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, PEA = phenylethylammonium.

Besides, the 2D perovskites exhibit special properties in comparison with their 3D analogous. Their natural quantum-well structure yields stable excitons, able to interact more strongly with phonons, spins and defects. Layered perovskites have been shown to be more structurally stable under non-ambient conditions than the 3D ones, with maintaining the same phase longer under increasing pressure or decreasing temperature^{33–35}. Temperature induced phase transitions are usually associated with the organic ions³³. These unique properties make 2D perovskites good candidates for new advanced materials for various applications³⁶.

The electronic properties of 2D perovskites have been repeatedly shown to be determined by the inorganic sublattice, while the organic cations demonstrate only indirect influence, such as steric effects^{25,37,38}. However, the nature of organic moieties does affect the crystal structure, including the crystal symmetry, bond length and bond angle, distortion of octahedra, and even the type of octahedra arrangement^{37,39,40}. These parameters are correlative with the electronic structure and optical properties. For instance, compounds with distorted octahedra have been demonstrated to exhibit a broader emission, that is explained by formation of trapped excitons due to higher

defect concentration^{37,39,41} or by self-trapping of excitons⁴⁰. Type of octahedral ordering affects the optical properties as well, thus compounds with face-shared octahedra have been shown to exhibit blue shifted bandgap, compared to corner-shared. Finally, dimensionality, particularly the value of n in $R_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, has been reported to dramatically affect its bandgap due to variations in quantum confinement.

Besides the correlation of optical properties with the crystal structure under ambient conditions, evolution of the properties at low temperature and under high pressure is of interest for several reasons. First, varying temperature and pressure allows to tune physical and chemical properties. Second, since device applications may require non-ambient conditions, the structural stability of the materials needs to be investigated. Finally, hydrostatic pressure is an alternative to chemical pressure, and useful findings under pressure may be further pursued in new compounds and technologies.

In summary, the importance of the organic cation nature in 2D perovskites has been repeatedly demonstrated, but organic cation composition-structure-properties relation in this class of materials has not been systematically studied. Particularly, the effect of hydrogen bonding and order-disorder conditions, although it has been widely discussed in 3D counterparts (which only have short organic groups)^{42–44}, is unclear in 2D perovskites. Tuning the organic cation size in order to adjust the electronic structure through quantum and dielectric confinement has not been systematically studied yet. Another open question in the 2D perovskites field is related to the strong natural anisotropy in this class of materials. Although the difference between the in-plane and out-of-plane directions is obvious and has been known for a long time³³, the relation between the degree of the mechanical anisotropy and optical response has not been investigated. Finally, the in-plane anisotropy, known in the other 2D materials, has not been demonstrated in the 2D perovskites.

The aim of my PhD thesis is to determine how physical (including optical) properties and the crystal structure of 2D hybrid lead-iodide perovskites ($R_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$) are dependent on composition (R , n). We aim to address the following questions:

1. How do hydrogen bonding and organic cations (including both methylammonium and the long interlayer cations) dynamics correlate with the optical properties in Huddleston-Popper perovskites?
2. How can the nature of the organic cation affect structural stability and disorder in two-dimensional perovskites?
3. What is the origin of the optoelectronic anisotropy in a 2D perovskite with corrugated inorganic layers?

To answer these questions, we use three main optical spectroscopic techniques: photoluminescence (PL), optical absorbance and Raman spectroscopy. When needed, supplementary methods such as, X-ray diffraction, nuclear magnetic resonance, differential scanning calorimetry, first principle calculations and electrical measurements were employed through collaborations. Most importantly, the choice of the materials was made to achieve the aim of the work. The multi-dimensional perovskite $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ containing two types of organic cations – a small methylammonium (MA) and a bulky phenylethylammonium (PEA), allowed us to study their dynamics and hydrogen bonding as an effect of dimensionality. Using a relatively short imidazolium-ethylammonium (ImEA) bication yielded the corrugated structure and so in-plane anisotropic $(\text{ImEA})[\text{PbI}_4]$ perovskite. The effect the barrier thickness and softness was studied in $(\text{HDA})_2[\text{PbI}_4]$ perovskite with a long flexible hexadecylammonium (HDA) cation.

Our work contributes to the knowledge of fundamental optical and physical properties of two-dimensional perovskites. We have shown how various modifications of the organic part causes changes in the properties and brings up a special feature for each of these materials.

The thesis consists of 8 chapters. Chapter 1 (Introduction) provides the general overview of the research area. It is also devoted to the identification of the research gap and purpose of the work.

Chapter 2 reviews the background and most important findings in the research area. They include the structural, electronic and optical properties of various 2D perovskites. Special attention is paid to the excitonic effects, such as trapping and

exciton-phonon coupling. We also review the structural stability of 2D perovskites and their response to non-ambient conditions.

In Chapter 3, the experimental techniques used in the work are described, namely absorption, reflection, photoluminescence, and Raman spectroscopy. For each the theoretical background and experimental setups are presented. Besides, the working principle of the in-situ high pressure and low temperature measurements are described. Finally, the synthesis methods of 2D perovskites are provided in this chapter. However, the detailed descriptions of the experimental procedures are given in the following chapters.

In Chapter 4 we report the optical characterization of $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ (phenylethylammonium - methylammonium lead iodide) perovskite in a wide temperature range in connection with methylammonium state, investigated by Raman spectroscopy. We report changes in optical properties, starting below 200 K and related to formation and strengthening of hydrogen bonding. Thus, methyl ammonium dynamics is important even in 2D perovskites with a smaller portion of MA ions.

Chapter 5 is devoted to the in-plane anisotropic $(\text{ImEA})[\text{PbI}_4]$ perovskite which combines the unique properties of hybrid halide perovskites and in-plane anisotropic potential of two-dimensional materials. We demonstrate strong in-plane anisotropy of the optoelectronic properties: photoconductivity, the band structure, the complex dielectric constant, and the vibrational modes. Using temperature-dependent analysis of the photoluminescence spectra, we confirm the anisotropic exciton-phonon coupling, which contribute to the shift of the photoluminescence peak maximum.

Chapter 6 investigates the high-pressure response in $(\text{HAD})_2[\text{PbI}_4]$ perovskite. Using the in-situ optical techniques – photoluminescence, transmission and Raman spectroscopies we investigate the evolution of the crystal and its electronic band structure under compression in the range 0-20 GPa. PL mapping identifies the domains exhibiting photoluminescence associated with variations in crystal structure due to softness and flexibility of the organic cation.

The findings are summarized and concluded in Chapter 7. The outlook of the possible future work is also provided in this chapter.

Chapter 2

Methods and Materials

2.1. Optical Techniques

2.1.1. Raman Spectroscopy

Raman Spectroscopy is a spectroscopic technique based on the effect of inelastic scattering of monochromatic light. The phenomenon was discovered by Chandrasekhara Venkata Raman in 1928, and earned him a Nobel Prize in Physics in 1930. The technique is widely used to identify the vibrational modes in molecules and crystals.

In contrast with real absorption, during scattering, the “excitation” puts the molecule into a virtual energy state for a much shorter time. This virtual state is not related to any electronic levels but to the induction of the electrical dipole moment in a molecule placed into electrical field created by electromagnetic radiation. The induced dipole moment depends on the electrical field (of frequency ν_0) and to the polarizability of the molecule, with the latter one being related to the vibrations of the chemical bonds (of frequency ν_{vib})⁴⁵:

$$\mathbf{p} = \mathbf{p}(\nu_0) + \mathbf{p}(\nu_0 + \nu_{vib}) + \mathbf{p}(\nu_0 - \nu_{vib}). \quad (2.1)$$

The first term describes elastic Rayleigh scattering, the second and the third ones correspond to Raman scattering, anti-Stokes and Stokes respectively. Figure 2.1 demonstrates a schematic diagram of the vibrational levels involved in the scattering process. In case of Stokes Raman scattering, relaxation happens to one of the excited vibrational states, so the Raman signal has lower frequency than the excitation light, and vice versa in case of anti-Stokes – the scattered light appears at the higher frequency range.

As Raman spectroscopy is usually used to determine the vibrational frequencies, Raman spectra are plotted as a function of Raman wavenumber or Raman shift – a difference in frequency between the incident (wavelength λ_0) and scattered light (λ_s) – expressed in cm^{-1} :

$$\Delta\nu = \frac{1}{\lambda_0} - \frac{1}{\lambda_s}. \quad (2.2)$$

Figure 2.1. Illustrations of the scattering types. Elastic Rayleigh scattering: photon energy E_0 does not change. Inelastic Raman scattering: energy of the scattered photon is decreased (Stokes) or increased (anti-Stokes) by a phonon.

Raman and Infra-Red (IR) Spectroscopies are two complimentary methods, both targeted to investigate the vibrational states of the materials. However, they are based on the different physical phenomena – inelastic scattering and absorption of infra-red radiation respectively. Thus, they have different selection rules. Vibrations are IR-active if dipole moment changes during the vibration and are Raman-active when there is a change in polarizability. For example, the stretching mode in a homonuclear diatomic molecule, such as O_2 , is never IR-active, because the dipole moment is constant, but is Raman active, because elongation of the molecule during the vibration increases the polarizability⁴⁵.

The intensity of the Raman signal is a complex parameter, dependent on many factors. First, one should note that Raman scattering is a very weak phenomenon, millions of times weaker than Rayleigh scattering or photoluminescence. For this reason, Raman spectroscopy had been a limited technique until invention of the lasers. Intensive monochromatic laser radiation as a source used together with narrow notch filters made the signal reasonably intense and Raman spectroscopy is a widely available method now. Summing up, the intensity depends on instrumental related parameter (such as the intensity of the source of radiation, the analyzed volume, the detector efficiency, and the measurement geometry) as well as fundamental parameters such as excitation wavelength ($I \sim \lambda^{-4}$), temperature, and the direction of anisotropic molecules and crystals⁴⁵. Let us consider the last one in detail.

Group theory is a useful tool to analyze the Raman spectra in respect to polarization of the incident and detected light. First, it helps to identify whether the vibrations are Raman (IR) active^{46,47}. In practice, Bilbao crystallographic server is a convenient recourse for this purpose⁴⁸. Symmetry analysis based on the group theory play an important role in analysis of anisotropic Raman spectra. Symmetry of the particular mode defines its Raman tensor $\tilde{R}$, that is related to the intensity:

$$I \sim |e_i \cdot \tilde{R}|^2 \quad (2.3),$$

$$I(\parallel, \perp) \sim |e_i \cdot \tilde{R} \cdot e_s|^2 \quad (2.4),$$

where e_i and e_s are the electric polarization unitary vectors of the incident and scattered light, respectively. Equation 2.4 describes the case when the polarization of both the excitation and detection is linear, equation 2.3 corresponds to detection of randomly polarized light, excited linearly.

Raman scattering, along with the other optical techniques, can be used together with confocal microscopy, extending the capabilities of the methods. In confocal microscopy, both excitation and detection happen from a small area of the sample (Figure 2.2). This is achieved by focusing a laser into a spot on the sample surface and detecting the signal from this spot only through a pinhole before the detector. Scanning the sample point by point and line by line allows obtaining Raman (or, alternatively, photoluminescence) images with high image contrast and resolution depth⁵¹.

Figure 2.2. Scheme of a confocal Raman Microscope.

The schematic of the Raman confocal microscope (based on Witec Alfa) is shown in Figure 2.2⁵¹. The WITec alpha 300RAS confocal Raman microscope coupled with an Acton spectrometer (possible diffraction grating of 150, 600 and 1800 grooves/mm) and a thermo-electrically cooled Andor CCD detector and three excitation lasers (633 nm, 532 nm and 457 nm) was used for the experiments. The optical fiber in the detection path does not conserve the polarization, so the detection efficiency is equal for any signal. Raman experiments were also conducted by inVia confocal Raman microscope with a diffraction grating of 1200 grooves/mm. Sections 4.4, 5.4 and 6.4 contain detailed information on the experimental conditions, such as laser power, integration time, etc.

2.1.2. Reflectance spectroscopy

Light interacts with solids in several ways: it can be reflected, transmitted, can propagate into the matter, being scattered, refracted, absorbed and then emitted. Reflection, transmission and abortion are related to each other and defined by the complex refractive index:

$$\tilde{n} = n + i\kappa, \quad (2.5)$$

where n , the real part, is refractive index, κ , the imaginary part, is called extinction coefficient and is related to the absorption coefficient α :

$$\alpha = \frac{4\pi\kappa}{\lambda}, \quad (2.6)$$

Reflectivity R can be expressed by Fresnel formula:

$$R = \left| \frac{\tilde{n}-1}{\tilde{n}+1} \right|^2 = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}. \quad (2.7)$$

In the classical model, electromagnetic radiation propagating through the medium resonantly interacts with oscillators. Atomic (bound electron – atom) dipoles, vibrational (atoms in a molecule or a crystal) and other types of oscillators can be observed in materials. Let us briefly review the atomic oscillators in the Lorentz model.

Electromagnetic radiation induces forced oscillation of the atomic dipole. If the frequency of the wave ω is far from the natural oscillator frequency ω_0 , its contribution to the dipole moment is small, and there is no absorption; near the

resonance the contribution to the dielectric constant is significant. Its real (ϵ_1) and imaginary (ϵ_2) part can be described by the equations:

$$\epsilon_1(\omega) = 1 + \chi + \frac{Ne^2}{\epsilon_0 m_0} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma \omega^2} , \quad (2.8)$$

$$\epsilon_2(\omega) = \frac{Ne^2}{\epsilon_0 m_0} \frac{\gamma \omega}{(\omega_0^2 - \omega^2)^2 + \gamma \omega^2} , \quad (2.9)$$

where γ is the dumping parameter, it causes the broadening and reflects the interactions with phonons, χ is the electric susceptibility and accounts for all non-resonant contributions to the polarizability of the atoms; N is the number of atoms per unit volume, e and m_0 – the electron charge and mass. In case if there are several oscillators (for example, excitons), the total complex dielectric function can be calculated as a sum of dielectric functions of j oscillators with oscillator strength f_j :

$$\epsilon_r(\omega) = 1 + \frac{Ne^2}{\epsilon_0 m_0} \sum_j \frac{f_j}{\omega_j^2 - \omega^2 + i\gamma \omega} . \quad (2.10)$$

The real and imaginary part of the dielectric function (and the refractive index) are not independent parameters. Having applied the law of causality (that an effect may not precede its cause) and complex number analysis, the relation can be expressed by Kramers-Kroing (KK) relationship⁵²:

$$n(\omega) = 1 + \frac{2}{\pi} \text{P} \int_0^\infty \frac{\omega' \kappa(\omega')}{\omega'^2 - \omega^2} d\omega' , \quad (2.11)$$

$$\kappa(\omega) = -\frac{2}{\pi \omega} \text{P} \int_0^\infty \frac{\omega' [n(\omega') - 1]}{\omega'^2 - \omega^2} d\omega' . \quad (2.12)$$

Combined with equation 2.7, KK analysis of reflectivity spectra allows to obtain the absorption coefficient. In practice it is not a trivial task, particularly the precise KK analysis requires a reflectivity data recorded at a wide frequency range. Several models have been proposed to fit the reflectivity spectra.

In this work, to analyze the reflectivity spectra, collected with a halogen lamp (15 V, 150 W, 2700 K) as the white light source using the Witec Raman microscope in back-scattering geometry (as in Figure 2.2), we applied the method of the KK-constrained variational fitting proposed by Kuzmenko⁵³, using the RefFIT software to obtain the dielectric constants and the absorption coefficient. The method is based on

analysis of the reflectivity by fitting it with the Fresnel equation (eq. 2.7), using some model function that satisfies the KK-relation as the dielectric function. In general, we have to use a function with many parameters to estimate the dielectric function. For example, we can try to use a superposition of a big number of the Lorentz oscillators (eq. 2.10) to obtain a good fit of the experimental data. However, this approach meets disadvantages: the number of oscillators (N) is unknown, the initial parameters are difficult to guess (especially for a great number of components), and finally, the number of parameters is more than $3N$, that makes them dependent on each other. To improve fitting, in the variational method the oscillators frequencies are equally spaced and fixed, their linewidths are equal and also fixed, and only the spectral weight of each oscillator is variable. In this approach a triangle shape is more convenient to use than the Lorentzian, as the latter has “tails”. The variational method has demonstrated a good approximation of the dielectric functions of various materials⁵³, but one should note that a wide spectral range of the experimental data is required for the accurate results, and in general no extrapolation should be done.

2.1.3. Absorption spectroscopy

The easiest way to obtain absorption spectra is transmission spectroscopy. The Raman microscope, described above (Figure 2.2), can be used to obtain the transmission spectra, with the sample placed between the white light source and the spectrometer. Optical density OD, proportional to the absorption coefficient α , can be calculated as a negative logarithm of transmittance:

$$OD = -\log_{10} \left(\frac{I}{I_0} \right) = 0.434\alpha l, \quad (2.13)$$

where I is the transmitted signal, I_0 is the signal from the light source. This approach is the most direct way to study the band structure of semiconductors. Reflection spectroscopy requires the complex analysis to separate the real and imaginary parts of the dielectric function. Photoluminescence involves more physical processes and its mechanism is more complicated. We will discuss it in the next chapter.

Absorption spectroscopy is the easiest way to determine the band gap in semiconductors; a Tauc plot is usually used for this purpose. Absorption spectra are plotted as $(\alpha\hbar\omega)^2$ vs $\hbar\omega$ (photon energy) for the direct band gap and as $(\alpha\hbar\omega)^{\frac{1}{2}}$ vs $\hbar\omega$ for the

indirect band gap semiconductors. Extrapolating the linear part of the slope to the x -axis yields the energy of the optical band gap. The method is also widely used to describe optical properties of the amorphous materials⁵⁴.

2.1.4. Photoluminescence Spectroscopy

The scheme of the light absorption-emission process in a direct band gap semiconductor⁵² is presented in Figure 2.3. Photons from the excitation source (a laser) are absorbed by the material, creating free carriers – electron-hole pairs. Initially, their energy is greater than the band gap, and they rapidly non-radiatively relax to the bottom of the conduction band (and the top of the valence band for the holes) emitting phonons so the energy and momentum conservation laws are followed. This process typically happens in $\sim 10^{-13}$ s, that is much faster than the radiative recombination that normally happens in the nanosecond range. Once relaxed, the electron-hole pair can recombine either radiatively, emitting a photon, or non-radiatively. Besides, there may be the intra-band gap states, both radiative and non-radiative, corresponding, for example, to excitons, trapped or self-trapped charge carriers.

Figure 2.3. Scheme of the photoluminescence process.

In this work, photoluminescence spectroscopy was applied to study the excitonic properties of two-dimensional hybrid perovskites. The photoluminescence spectra and photoluminescence mapping images were recorded with the confocal Raman microscope (Figure 2.2). The set up allowed to record the spectra in-situ in a wide temperature range (78-370 K in this work) and under high pressure up to 25 GPa. The description of these techniques is presented in the next chapter. The detailed conditions of the experiments, such as excitation wavelength and laser power are presented in sections 4.4, 5.4 and 6.4.

2.2. In-situ measurements under high pressure and low temperature

2.2.1. Diamond Anvil Cell

Applying high pressure is a relatively rare method so it requires an additional description of its motivation and technical details. First, one should note that the high pressure applied in material physics is in the range from ~ 0.1 GPa and up to 100 GPa or even more, that is in the order of a million of atmospheres. Obviously, such conditions are hardly achieved on the Earth surface or in technology and can only be found in the center of our planet. However, such extreme conditions provide is a powerful tool to tune the crystal structure and properties of the material significantly and so to create a perfect system for investigating the composition – structure – properties relations. Achieving the special phenomena and understanding their mechanisms under high pressure provides a reasonable guideline for engineering materials with the desirable properties.

Figure 2.4. a) A photograph and b) a scheme of a Mao - type diamond anvil cell (DAC).

In practice, a diamond anvil cell (DAC) is the most convenient tool to achieve the pressure in the range up to 100 gigapascal for optical and electrical measurements. A photo and a scheme of a MAO-type DAC (similar to the one used in this work) is shown in Figure 2.4. The sample, pressure transmitting medium and a ruby crystal are placed in a chamber formed by a gasket and two diamonds (sometimes sapphires) on the top and the bottom. The compression is achieved by pushing the diamonds towards each other while tightening the screws (Figure 2.4.a). Choice of the pressure medium depends on the experiments, normally it is silicon oil or sodium chloride and is used to achieve the hydrostatic pressure. The material itself can play this role as well if tightly packed into the chamber. Ruby is used as a reference to measure the current pressure. It has the well-known dependence of its photoluminescence (PL) wavelengths on pressure which can be calculated by the following equation:

$$P(\text{GPa}) = \frac{A}{B} \left(\left(\frac{\lambda}{\lambda_0} \right)^B - 1 \right), \quad (2.14)$$

where $\lambda_0 = 694.24$ nm at 298 K – the PL peak position at ambient conditions, λ is the PL peak position at the given pressure; A is equal to 1876 and B is equal to 10.71 according to the work by A.Chijioke⁵⁵.

Such DACs allow conducting optical spectroscopy measurements, such as Raman, PL and transmission. Besides, it can be used in a confocal microscope. The detailed description of the high-pressure experiments is presented in section 6.4.

2.2.2. *Liquid nitrogen flow stage*

Temperature dependent measurement were conducted with a Linkam THMS600 temperature microscope stage (Figure 2.5). It allows heating and freezing of the sample in the range from -195°C to 600°C. The temperature variations are achieved by flow of liquid nitrogen to cool and electrical heating. The sample is placed in the hermetically sealed chamber and kept under nitrogen atmosphere or vacuum to avoid condensation of the water vapor from air.

In this work, Linkam stage was used to investigate the evolution of the optical and vibrational properties of 2D perovskites in the temperature range between 78 K and 293 K. The stage was assembled with the Witec confocal Raman microscope.

Figure 2.5. Linkam THMS600 Temperature microscope stage.

2.3. Synthesis methods

First, a brief overview of the most frequently used approaches to synthesize 2D perovskites is provided.

One of the oldest methods is the silica gel technique, used by Ishihara in the first works on alkylammonium 2D perovskites. The idea of the method is a diffusion of cations through the gel for a very slow rate of crystal growth^{56,57}. However, the crystals obtained by the gel method are easily contaminated and it is quite difficult to control the gel hardness³³. Another way to obtain the crystals (more appropriate for a shorter chain: butyl or hexyl ammonium) is slow evaporation of an aqueous solution of the precursors⁵⁷. Ishihara also proposed to use a mixture of acetone and nitromethane as a solvent for the reaction. This method allowed to obtain a higher member perovskite ($n = 2$ phenyl ethyl ammonium lead iodide) as well⁵⁸.

Nowadays the aqueous solution crystallization method is normally applied to obtain crystalline samples of the Ruddlesden-Popper series. Stoichiometric amounts of PbO (or PbI₂), RI, MAI are dissolved in a mixture of aqueous HI and aqueous H₃PO₂ during boiling. Slow cooling to room temperature yields uncontaminated single crystals of the 2D perovskites - iodides^{17,59–61}. Dion-Jacobson⁶² and alternative cation perovskite⁶³ phases were obtained by similar HI solution method. This method is suitable for the rarer $\langle 111 \rangle$ oriented perovskites⁶⁴.

Bromide perovskites⁶⁵ were crystallised from aqueous HBr solution using similar approach (no H_3PO_2 is necessary). Alkyl ammonium lead bromides can be obtained by another solution method as well: antisolvent acetone is to be added to DMF solution of precursor⁶⁶.

The aqueous solution method was used for preparation of tin-based perovskites. Since Sn^{+2} tends to be oxidised to Sn^{+4} , oxygen-free atmosphere is recommended, although Cao et. al. reported that presence of H_3PO_2 is enough to prevent oxidation⁶⁷.

Figure 2.6. 2D perovskite thin platelets, obtained by a) mechanical exfoliation of a single crystal (adapted with permission from reference 72; and b) by dropping a very dilute DMF-chlorobenzene precursor. Adapted with permission from reference 76.

Spin-coating is an extremely important process for cheap and easily prepared devices, and good quality 2D perovskites films can be formed. Precursors^{26,68–70} or solution of the final bulk material⁶⁶ in DMF or DMSO is usually used for spin coating, followed by annealing at 100 °C. Some authors recommend to carry out spin coating in a glove box with oxygen and moisture levels <0.1 ppm⁶⁸. For tin-based perovskites, DMF and DMSO solutions of bulk material were used for spincoating⁶⁷. MACl can be added to the precursor solution to improve morphology of the films which have been used for perovskite solar cells⁷¹.

For fundamental studies of the materials, high quality thin crystals are often needed (Figure 2.6). Mechanical exfoliation, similar to that used in exfoliating graphene, is the easiest way to obtain thin (up to a monolayer) crystals due to weak interlayer bonding of the 2D perovskites^{72–74}. Chemical Vapor Deposition (CVD) method is known to yield high-quality nano-crystals as well as films. 2D perovskites can be obtained by this method where the source of heavy PbX_2 is placed closer to the deposition zone than the light organic halide⁷⁵. Another method to obtain nano-size platelets is dropping a very dilute DMF-chlorobenzene precursor solution on the

substrate followed by mild drying⁷⁶. Besides, nano-plates could be converted from spin coated film by vapour annealing⁷⁷.

Table 2.1. Summary of the 2D perovskite synthesis methods.

Method	Highlights	Reference
Silica-gel technique	A diffusion of cations through the gel for a very slow rate of crystal growth.	56,57,33
Crystallization from organic solutions	Based on good or poor solubility in different organic solvents. Mixture of acetone (good solvent) and nitromethane (anti-solvent).	57,58
Crystallization from aqueous HI or HBr solution	The crystals grow during slow cooling. This is the most used method nowadays. Suitable for majority of the 2D perovskites	57, 17,59–61-67
Spin-coating	Perovskite thin films from DMF or DMSO solutions	26,68–70-71
Mechanical exfoliation	Thin crystals with good surface quality	72–74
Nanocrystals	Various methods such as CVD, drop-casting and vapor annealing of spin-coated films for high-quality nanocrystals	75-77

Chapter 3

Background and Literature Review

3.1. Introduction

In this Chapter, the publications on the structural, electronic, and optical properties of 2-dimensional hybrid halide perovskites under ambient condition, high pressure and various temperatures are summarized. The review is organized in the following way: first, structural features of 2D perovskites are discussed. Second, electronic and optical properties of various compounds are presented. Then the excitonic effects, such a coupling and trapping is reviewed in detail. Finally, we analyze structural stability of 2D perovskites, and the phenomena caused by applying non-ambient conditions.

3.2. Crystal structure, motifs and orientation in films

In case of regular 3-dimensional perovskites, the sizes of the A , B and X ions are to fit the certain ratio to form perovskite-like structures. The ability to form a perovskite-like structure is determined by the Goldschmidt tolerance factor t ^{78,79}:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}. \quad (3.1)$$

For perovskite-like 3D crystal structures, the Goldschmidt Tolerance Factor usually is $0.8 < t < 1$ ⁷⁸, that strictly limits the radius of the cation A .

For two-dimensional perovskites $R_2(A)_{n-1}M_nX_{3n+1}$, the same rule applies to the A cations. The rule is relaxed for the organic cation R , and R can take various values. R still needs to obey a few restrictions. Firstly, R must contain at least one terminal cation group, which can form hydrogen bonds with the inorganic anions. Usually, one or two protonated terminated amines take part in forming hybrid layered structures. Secondly, the size and shape of the organic molecule R influence the formation of the layered structures. The molecular cross-section (the projection down the long axis of R) must be approximately equal to the area between terminal halides of the inorganic framework. In case of lead iodide, this is a square of $\sim 40 \text{ \AA}^2$. However, the length of the organic cation R can take on a wide range of values. In fact, it just needs to be longer

than the size of the vacancy between inorganic octahedra²⁵ to prevent the formation of 3D perovskites.

Moreover, interactions between the *R* cations can stabilize or destabilize the structure due to Van der Waals, aromatic-aromatic π -interactions²⁵, and hydrophobic forces⁸⁰. It should be also noted that in contrast with disordered MA in cubic 3D structures²⁴, longer cations in 2D perovskites are in fact rigid due to van der Waals forces and in some cases π - π interactions³⁷.

The nature of *R* cation has been shown to significantly affect the structure of 2D perovskites^{25,37}. The layered hybrid perovskites with *R* = PhC_{*m*}H_{2*m*}NH₃ illustrate this phenomenon (Figure 3.1). Despite these cations apply to the same homologous series, the length of the alkyl part affects not only lattice parameters but also stoichiometry and ordering of the inorganic octahedra, including the direction of the planes and type of sharing. And this is not the only example of different types of octahedral ordering. In general, the case where the octahedral layers are flat and located along <001> plane is the most common type^{25,81}. Alkylammonium metal halides are the most common examples, in which the compounds with the general formula C_{*x*}H_{2*x*+1}MX₄ (where *x* = 4-10, *M* = Pb, Sn, Ge, *X* = Cl, Br, I)^{34,76,82-84} have been reported to exhibit the <001> arrangement of octahedra as well as their solid solutions with various concentrations of Cl/Br/I components^{85,86}. Another group of compounds, known to be of this type, are phenylethyl ammonium metal halides^{87,88}. Histammonium and benzylammonium lead and tin iodides has been reported to follow the <001> structure type as well⁸⁹.

The <110>-type of layered perovskites is less common. Compounds containing the iodoformamidinium cation are of this type^{25,81,90} as well as compounds with two ammonium groups in the organic cation. For example, α -(DMEN)PbBr₄ (2-(dimethylamine)ethylamine) is known to be a “3 × 3” <110> perovskite. Local hydrogen bonding of the “chelating” effect causes the unique bending of the inorganic layers⁴¹. In this case, the corner shared octahedra layers form folds, and 3 × 3 means that the width of the folds is equal to 3 octahedra. However, many of the perovskites with two amino groups do not follow this rule, for instance, (EDBE)PbCl₄, H₃N(CH₂)₆NH₃PbBr₄, and (AEQT)PbBr₄ (AEQT) = 5,5'''-bis(aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene) are <100> while (EDBE)PbBr₄ is <110> (EDBE = 2,2-(ethylenedioxy)bis-(ethylammonium))^{40,91-93}. The compounds, containing

cyclohexylammonium cation, are known to form <111>-oriented 2D perovskites. Moreover, there are some exotic types of layering⁸¹.

Figure 3.1. Structural motifs of the RBPb_xI_y layered perovskites. a) Structure of $\text{PhCH}_2\text{NH}_3\text{-PbI}$ and $\text{PhC}_2\text{H}_4\text{NH}_3\text{-PbI}$. b) Structure of $\text{PhC}_3\text{H}_6\text{NH}_3\text{-PbI}$. c) Structure of $\text{PhC}_3\text{H}_6\text{NH}_3\text{-PbI}$. b) and c) Structures contain both face-sharing and corner-sharing octahedra; a) Structures contain only corner-sharing octahedra. Reprinted with permission from ref. 37 Copyright (2016) American Chemical Society.

One more class of 2D perovskites is worth to discuss. So-called “multilayered” or quasi-2D perovskites can be obtained from 3D compounds by substitution of the part of small A^+ cations with a longer R^+ one^{23,24}. Thus, these materials contain both A^+ and R^+ cations. The generic chemical formula of the multilayered perovskites is $\text{R}_2(\text{MA})_{n-1}\text{Pb}_n\text{X}_{3n+1}$, where R is a monobasic amine; X is halide; and n represents a number of octahedral layers within one inorganic sheet. The most common 2D perovskites contain methylammonium (MA), lead (Pb), but the tin-based⁹⁴ and formamidinium-based⁹⁵ multidimensional perovskite have been described as well.

Figure 3.2. Examples of Dion-Jacobson DJ (a), Ruddlesden-Popper RP (b), and alternating cations in the interlayer space (ACI) (c) 2D perovskite phases. Adapted with permission from reference 96 (a, b) and 63 (c). Copyright (2017, 2018) American Chemical Society.

Depending on the type of the organic cations and relative stacking of the inorganic layers, all <100> oriented layered hybrid organic-inorganic perovskites can be divided into four categories: Dion-Jacobson – DJ (Figure 3.2a)^{62,97}, Ruddlesden-Popper – RP (Figure 3.2b)⁸⁰, perovskites with alternating cations in the interlayer space – ACI

(Figure 3.2c)⁶³, and Aurivilius - AV⁶³ (known only among oxide perovskites) phases. RP perovskites contain a pair of monobasic ammonium (R^+) and offset stacking of the inorganic layers along the both a and b directions⁸⁰. DJ perovskites, containing one interlayer dibasic ammonium cation (R^{+2}), can form layers arranged one strictly above the other⁶², or shifted by a half of the octahedron along only a or b direction⁹⁷. The phase with alternating cations in the interlayer space is similar to DJ perovskites in terms of the displacement of the inorganic layers only along one of a or b directions. However, this class contains two types of the organic cations in the interlayer space. ACI perovskites were reported to exhibit decreased band gap in comparison with the PR analogous⁶³.

Out-of-plane charge transport in layered perovskites is significantly obstructed, therefore the orientation of thin films plays a critical role in application of 2D perovskites. The compounds with small values of n demonstrate high degree of inorganic octahedral sheets parallel to the substrate surface⁹⁸. For instance, in the methyl-butylammonium perovskite series only the $n = 1$ member tends to grow with its inorganic planes parallel to substrate surface, while $n = 2$ grown with the octahedral planes parallel to the substrate as well as along other directions. The perovskites with $n \geq 3$ tend to grow vertical layers^{23,99}, and this has been explained by the preferential growth at the liquid–air interface of the precursor solution, regardless the roughness or material of the substrate¹⁰⁰.

Vertically grown inorganic layers were shown to dramatically improve solar cell performance of the Ruddlesden-Popper phase perovskite thin films¹⁰⁰. A few methods to improve crystallinity and degree of the vertical orientation were proposed. First, adding NH_4SCN and NH_4Cl to the precursor solution was shown to tune the orientation and to decrease concentration of nonradiative defects yielding 14.1% PCE for the $n = 5$ methyl-phenylethyl-ammonium perovskite¹⁰¹. The second way to improve orientation and crystallinity is to produce films by hot-casting instead of conventional spin-coating²⁸. Varying solvents may help as well, for instance better films of the hot-casted $n = 5$ buthyl-based perovskite were obtained from 3:1 DMF:DMSO solution than from the pure DMF or DMSO alone. The nature of the organic cation was shown to affect the orientation as well, for instance substitution of n -buthylammonium with *iso*-buthylammonium produces $n = 4$ perovskites with better vertical orientation of the

films⁶⁸. In contrast with the mentioned above $n = 3$ RP perovskites, as well as the DJ perovskites⁶², the $n = 3$ ACI perovskite grows in preferred horizontal orientation⁶³.

3.3. Stability

The main advantage of 2D perovskites over their 3D counterparts is the stability of thin films under illumination at ambient conditions. Encapsulated 2D perovskite-based solar cells retained 60% of their efficiency after an aggressive test: illumination of 100 mW/cm² for duration of 2250 h; and they were also shown to be much more moisture stable than the 3D perovskites. Higher members of quasi-2D perovskite family were shown to be good candidates for photovoltaic applications due to their stability as well¹⁰².

Even the addition of a small amount of 2D perovskites may yield an outstanding increase in the long-term stability of the all-inorganic 3D perovskite. Moreover, CsPbI₃×0.025 EDAPbI₄ (EDA = ethylenediamine) perovskite thin film showed a PCE of 11.8%, that was a record for all inorganic perovskite solar cells, due to effective electron transfer and passivates the surface defects¹⁰³. Presence of butylphosphonic acid 4-ammonium chloride was demonstrated to increase both the solar cell PCE and stability of MAPbI₃-based devices as well¹⁰⁴.

Treatment of the 3D perovskite surface with 2D perovskite was shown to be a good approach for more stable devices. 2D/3D interface HOOC(CH₂)₄NH₃)₂PbI₄/MAPbI₃ demonstrated ultra-stability and good performance¹⁰⁵. Addition of buthyl ammonium to the surface of FA/Cs-based collar cell gave the similar outstanding improvement of stability³².

3.4. Electronic structure

Low dimensional perovskites exhibit the special properties due to their unique structure. The HOMO-LUMO energy gap of the organic molecules is usually much higher than the band gap of the inorganic layer⁹³. Thus, natural multiple quantum-well structures are formed and the quantum confinement effect takes place due to low dimensionality of the semiconductor layers (potential walls), confined between

optically inactive organic spacers (barriers)^{37,80,106,107}. Quantum confinement depends on thickness of the quantum well and of the barrier, for example dimensionality, particularly the value of n in $R_2(\text{MA})_{n-1}\text{Pb}_n\text{X}_{3n+1}$ has been reported to dramatically affect its bandgap. Thus, the band gap and excitonic binding energy decrease when the parameter n increases²³.

Dielectric confinement should be considered along with the quantum confinement: the large difference between the dielectric constants of the organic barrier and the semiconducting layer is the additional enhancer and stabilizer of the excitons due to an image-potential-magnified attraction of charged particles (image charge effect)^{108–110}.

The quantum and dielectric confinement result in two main consequences. The first is the increased bandgap (and change of the form of the density of states)⁵². For instance, the band gap of the three dimensional MAPbI_3 is 1.51–1.61 eV^{6,23,37}, while the bandgap of the layered $(\text{PEA})_2\text{PbI}_4$ is 2.22–2.24 eV^{23,37}. The second consequence is generation of stable excitons. Excitons are generally classified into two main classes: Frenkel or small excitons and Wannier or large excitons. The radius of small excitons is smaller than the unit cell parameters, that of Wannier excitons is larger. 3D hybrid perovskites were shown to form large excitons with binding energy E_b of 4–50 meV and radius of 2.2–3.8 nm. Small excitons with $E_b = 500 - 1000$ meV were found in various organic materials^{52,81}. 2D perovskites exhibit strong excitonic absorption and luminescence even at room temperature. Excitonic binding energy was found to be 320 meV for $(\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{PbI}_4$ (and was shown to increase with the length increasing)³³, 220 meV for PEA_2PbI_4 and 170 meV for $\text{PEA}_2\text{MAPb}_2\text{I}_7$ ¹⁰⁹. However it is not possible to classify the excitons in 2D perovskite based on the above simple classification. Some phenomena can be better explained by the model for Frenkel excitons, while the actual radii of the excitons are comparable to the unit cell size. In practice this yields a strong sharp exciton luminescence and absorption even at room temperature^{56,80,106} with short lifetimes (tens of picoseconds)^{61,111}.

Besides, improved enhancement of optical nonlinearity has been shown in buthyl-methyl ammonium Ruddlesden-Popper series in comparison with the analogous. The 2D perovskites exhibited four times increase of third harmonic generation due to quantum confinement¹¹².

In general, theoretical models for first-principle calculations relevant to 2D hybrid organic-inorganic perovskites are much less developed than that of the 3D ones, and they require significant computational resources due to a very large number of atoms per unit cell. A detailed review of theoretical models for 2D perovskites is presented by Laurent Pedesseau et. al.¹². Models based on an ultrathin quantum well with finite confinement barriers are shown to be applicable, detailed theoretical discussion of quantum confinement in 2D perovskites is published in reference¹¹³.

The electronic structures of 2D perovskites have been repeatedly shown to be mainly dependent on the inorganic sublattice, while organic cations demonstrate only indirect influence, such as steric effects^{25,37,38}. The top of the valence band has been reported to be determined by Pb 6s and I 5p orbitals and the bottom of the conduction band by Pb 6p and I 5s ones³⁸. However, the nature of organic cations has been found to significantly affect the crystal structure, including the crystal symmetry, bond length and bond angle, distortion of octahedra, and even the type of octahedra arrangement^{37,39,40}. These parameters have been shown to be tightly correlated with the electronic structure and optical properties. Bond contraction causes decrease of bandgap due to greater orbital overlap¹¹⁴. Octahedral rotation induces weaker overlap and hence blueshift of bandgap^{37,114}. Compounds with distorted octahedra have been shown to exhibit a broader emission, that is explained by formation of trapped excitons due to higher defect concentration^{37,39,41} or by self-trapping of excitons⁴⁰. The type of octahedral ordering affects electronic structures as well, thus compounds with face-shared octahedra have been shown to exhibit blue shifted bandgap, compared with the corner-shared one, due to additional quantum confinement¹¹⁵.

The above described quantum well model, that is hardly dependent on the organic cations, is true for most of 2D perovskites due to the large HOMO-LUMO gap of the organic cations. However, some compounds containing special functional organic molecules are exceptional cases. For example, introducing dye molecules into the structure as inorganic counter ion have been reported; 2D 5,5'''-bis-(aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene lead chloride exhibits emission was determined by the organic layer¹¹⁶. A similar effect was shown for naphthalene -based 2D perovskite, where efficient energy transfer from the inorganic to organic layer was observed, followed by naphthalene phosphorescence¹¹⁷. Introduction of some other opto-

electronically active cations led to the formation of 1D or 0D perovskites, while electronic coupling between the organic ions and the inorganic lattice was kept strong^{118,119}.

Sudeep Maheshwari et. al. introduced electron donating and electron withdrawing organic cations, resulting in the optical band gap determined by both the inorganic PbI_4 and organic molecule¹²⁰. The band gap of electron donating 2,7-dibutylammonium[1]benzothieno[3,2-b]-[1]benzothiophene (BTBT) turned out lower (1.66 eV) than that of the other 2D perovskites. Introduction of electron withdrawing groups, such as *N,N*-bis(*n*-butylammonium)- perylene-3,4,9,10-tetracarboxylic diimide (PDI), led to the much lower band gap of 0.11 eV. These results were obtained by calculations¹²⁰.

The organic layer may also affect the dielectric confinement that can be decreased by introducing highly polarizable molecules. For instance, incorporating iodine molecules was shown to affect the electronic structure and optical properties of 2D perovskites significantly through decreasing the dielectric effect, resulting in a decrease in exciton binding energy to 50 meV¹¹⁰. Similar results were obtained by introducing highly polarised organic molecule, containing hydroxy group, as organic layer, e.g., the exciton binding energy of $(\text{HOCH}_2\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ was found as low as that of 3D perovskite (13 meV)¹²¹. Reduced interlayer distance (2 Å) by using a short propane-1,3-diammonium bication allows to minimise quantum confinement as well, significantly enhancing interlayer charge transfer³¹.

The fact that no interlayer electronic coupling was shown for conventional 2D perovskites (for example, alkyl ammonium or phenylethylammonium lead halides) and the quantum well structure implies that the band structure does not depend on number of layers, i.e. the optical properties of bulk 2D perovskite should not differ from that of a single layer sample. However, shift of the optical properties has been demonstrated for atomically thin $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ sheet (single or double layer) in comparison with the bulk crystal. The difference resides in an unusual structural relaxation leading to a blue shift of the band gap of the single layer sample by $\sim 5 \text{ nm}^{76}$.

3.5. Exciton-Phonon Interactions – Excitonic states in 2D perovskites

Optical properties of 2D perovskites are dictated by excitons, and that is why investigation of intrinsic and extrinsic, radiative and nonradiative exciton recombination pathways is essential. The intrinsic pathways are related to exciton-phonon interactions. Lattice vibrations create spatial and temporal potential fluctuations, where the first cause scattering of excitons and broadening of excitonic peaks in optical spectroscopy, while the second lead to the fine structure of the spectra, known as Frank-Condon shape. Besides, a moving exciton is able to create vibrations around it, inducing lattice distortions^{122(p. 203)}.

A few theories are used to describe the electron-phonon coupling. A model for the long wavelength acoustic phonons (LA) called “Deformation Potential” gives the best approximation for the short-range interactions of charges with local changes in the crystal potential caused by the vibrations. Electrons interact with the optical phonons (only LO) as well, due to the microscopic electric field fluctuations in polar crystals. The second mechanism called “Fröhlich interactions” implies a long-range force. Piezoelectric interaction and interaction with nonpolar optical modes are known as well but are not important for 2D perovskites¹²².

Exciton (electron) - phonon coupling is one of the reasons of emission spectra broadening. Dependence of full weight at half maximum (FWHM or Γ) of a PL peak on temperature allows extracting the coupling parameters and can be expressed by the following equation^{123,124}:

$$\Gamma(T) = \Gamma_0 + \Gamma_{ac} + \Gamma_{LO} + \Gamma_{imp} = \Gamma_0 + \gamma_{ac}T + \gamma_{LO} \frac{1}{e^{h\omega_{LO}/k_B T} - 1} + \gamma_{imp} e^{-\frac{E_b}{k_B T}}, \quad (3.2)$$

where Γ_0 represents FWHM at 0 K, which differs from zero due to the finite lifetime and inhomogeneous broadening caused by disorder and imperfections. Γ_{ac} and Γ_{LO} (homogenous) are caused by the exciton-phonon coupling with the acoustic and longitudinal optical phonon (of energy $h\omega_{LO}$, respectively; and the last term Γ_{imp} takes into account the exciton scattering (inhomogeneous) on ionized impurities with an average binding energy E_b . k_B is the Boltzmann constant, γ represents the exciton-phonon coupling strengths^{123,124}.

Figure 3.3. Functional form of the dependence FWHM on temperature in case of different contributions. Reprinted from ref. 123 with permission.

The terms Γ_{ac} , Γ_{LO} and Γ_{imp} give opposite contributions to the FWHM vs temperature plot (Figure 3.3). Thus, the shape of the graph indicates which coupling is stronger, and fitting the experimental data allows to extract the coupling strength constants.

2D hybrid perovskites have been repeatedly reported to exhibit strong exciton phonon coupling. Thus, γ_{ac} and γ_{LO} in 2D PEAPbI₄ (phenylethylammonium lead iodide) were found more than ten times higher than that in inorganic quantum wells¹²⁴. Electron-phonon coupling was shown to be highly related to the rate of free exciton (or free charge) trapping, affecting PLQY dramatically. For instance, exciton-phonon coupling in buthylammonium lead iodide were evaluated to be twice as strong as that in phenylethylammonium lead iodide, so the first exhibits a faster nonradiative decay time and lower PLQY¹²⁵.

Strong exciton-phonon coupling was shown for phenylethylammonium lead iodide by optical absorbance and photoluminescence spectroscopy at 15 K. At such a low temperature excitonic peaks split to a few peaks, separated by 40-43 meV due to exciton phonon coupling¹²⁶. Coupling to coherent phonons in the organic cations was observed for the same material by means of transient absorption spectroscopy¹²⁷.

When exciton-phonon interaction strength exceeds some critical value, excitons get immobilized, creating so called self-trapped excitons (polarons) as often occurs in polar semiconductors⁷³. Self-trapping exciton is an intrinsic phenomenon. If the

material also contains defects or impurities, excitons may bound to the defects, forming (extrinsic) trapped excitons. Moreover, excitons may be self-trapped near the defects, causing binding energy that differs from the intrinsic self-trapping. These three scenarios are schematically shown in Figure 3.4 and are described with examples below.

Figure 3.4. A) Self-trapped exciton; B) exciton, trapped by a defect; C) extrinsic self-trapping, affected by defects. The ball represents exciton, the surface is potential energy. Adapted with permission from reference 128. Copyright (2018) American Chemical Society.

Excitons in many 2D perovskites tend to bind to defects and impurities; radiative and nonradiative pathways taking place depending on the type of the defect (Figure 3.5). Different types of defects always form, caused by chemical impurities, vacancies, or faults. If the defect does not fit the parent lattice well enough, it induces a cloud of distorted host structure around the defect. Excitons can be trapped by this distorted structure, causing typical extrinsic luminescence. These excitons are called trapped or bound excitons. The energy of the photon, emitted from the bound exciton state, is always lower than that of the free exciton. The difference is equal to the binding energy between the exciton and the impurity. The value depends on the chemical nature of the defect, donor-acceptor behavior and charge^{129,130 (p 80;180)}.

Some 2D perovskites were shown to exhibit emission from trapped excitonic energy levels due to defects. Both shallow and deep trapped excitons were found in $(\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{PbI}_4$ ⁵⁷. The binding energy of shallow trapped excitons is not very high

and normally it yields radiative recombination from the trap level. The ratio of free and bound excitons increases with the increase of temperature, due to thermal energy activation⁵⁷. The same explanation of the additional red-shifted peak, more intense at low temperature, was provided for (PEA)₂PbI₄^{124,126}, (BA)₂(MA)_{*n*-1}PbI_{3*n*+1}⁸⁰, (BA)₂PbI₄ (shallow, neutral donor trapped excitons)²⁷, (PEA)₂(MA)_{*n*-1}PbI_{3*n*+1} (shallow defects)¹³¹. The formation of iodine-related shallow defects was proposed in low-dimensional perovskites in contrast with MA⁺-related defects in 3D perovskites. Moreover, large organic cations are able to suppress defects and hysteresis, which is useful for solar cell applications¹³¹.

Figure 3.5. Schemes of the radiative (a) and nonradiative (b) trapping of electrons (or excitons). Dash line represents nonradiative recombination pathways, the solid one corresponds to radiative recombination.

Deep trapping usually leads to nonradiative decay. Existence of exciton trapping was shown by Gauthron et. al. based on temperature dependent PL intensity in phenyl ethyl ammonium lead iodide. The obtained activation energy was far from reported exciton binding energy, besides being sample dependent, and was attributed to nonradiative defects-traps¹²⁴.

Another evidence of the trapped states was provided through power-dependent emission intensity. PL intensity grows in a power law function, $I_{PL} \sim I_{ex}^k$, where k is the power law coefficient, reflecting the recombination mechanism. In case of free exciton recombination $k = 1$, while presence of the trapped states yields $k = 1.5$, exhibiting saturation behavior at high excitation intensities^{132,133}.

Self-trapping of excitons leads to $k = 1$ and it does not exhibit saturation at high excitation intensities, because self-trapping is not limited by concentration of defects¹³⁴. Self-trapping causes temporal lattice deformation disappearing after exciton recombination. Self-trapping is schematically presented in Figure 3.4b¹²⁸. Scheme of electronic levels in case of self-trapping is presented in Figure 3.6. Luminescence from the self-trapped exciton (STE) states is normally broad and significantly red shifted from the free exciton peak. The decreased energy of the STE state and shape of the ground state (GS) contribute to the red shift, that together with the increased PL width leads to realization of white light emission¹²⁸.

Figure 3.6. a) Scheme of energy levels in case of self-trapped excitons. Emission (dash lines) occurs from free excitonic state (FE) and self-trapped excitonic state (STE). Red and blue lines represent self-trapping process with activation energy $E_{a,trap}$ and that of detrapping $E_{a,detrap}$. b) White light emission due to self-trapping from (N-MEDA)PbBr₄ (red) and (N-MEDA)PbBr_{3.5}Cl_{0.5} (black); the orange line is the Sun spectrum. Adapted with permission from ref. 128. Copyright (2018) American Chemical Society.

Some 2D perovskites have been reported to be white light emitters due to self-trapped excitons^{41,65,91,134–136}. Most of the perovskites exhibiting self-trapping form $\langle 110 \rangle$ -oriented perovskite sheets. They are 2×2 and (EDBE)PbBr₄⁹¹ (EDBE = 2,2-(ethylenedioxy)-bis(ethylammonium)), 2×2 (N-MEDA)PbBr₄ ((N-MEDA = N¹-methylethane-1,2-diammonium)¹³⁵, 3×3 α - (DMEN)PbBr₄ (DMEN = 2-(dimethylamino)ethylamine)⁴¹. A few examples of $\langle 100 \rangle$ white light emitting perovskites are known too: (EDBE)PbCl₄⁹¹, (C₆H₁₁NH₃)₂PbBr₄¹³⁶, and (*cis*-

CyBMA)PbBr₃ (*cis*-CyBMA = Cyclohexane-bis(methylamonium))⁶⁵. In all cases, the broad-band emission was explained by self-trapped excitons.

Besides the coupling to phonons and defects, two excitons can interact with each other due to the columbic forces, forming a so-called biexciton. Relatively high binding energy was shown for 2D perovskites (~40-70 meV for $n = 1$ and ~30 meV for $n = 2$)^{81,137}. Biexcitonic photoluminescence exhibits quadratic dependence of PL intensity on excitation power^{81,137}. Triexcitons were observed in 2D perovskites at high excitation powers as well (10^{12} - 10^{14} photons/cm²). Bilogarithmic power dependence was reported to have a slope of 2.6¹³⁸.

Although exciton binding energies in 2D perovskites are normally very high and the excitons hardly dissociate at room temperature, a special mechanism for exciton dissociation has been reported for thin films of higher ($n > 2$) members of Ruddlesden-Popper perovskites. Blancon et. al. demonstrated that excitons in (BA)₂(MA) _{$n-1$} PbI_{3 $n+1$} perovskites ($n = 3-5$), dissociate to long-live free carriers at the boundary edges, not losing the energy via nonradiative process and being able to contribute to photocurrent²⁹.

Besides the above listed excitonic effects, a few rarer phenomena have been observed in particular 2D perovskites. Specifically, Rashba band splitting (splitting of bands with different spins) has been demonstrated in noncentrosymmetric ($C2/m$) PEA₂MAPb₂I₇. Although the DFT calculations, giving this space group, are very sensitive and cannot prove the effect, photoluminescence lifetime of the $n = 2$ perovskite is much lower than that of centrosymmetric $n = 1$ or $n = 3$ perovskites, indicating slow indirect thermally activated recombination from the split levels⁶¹. Two more 2D perovskites have been observed to crystallize in noncentrosymmetric space groups: (PhMe-NH₃)₂PbCl₄ ($Cmc2_1$)^{12,139} and (CH₃NH₃)₂Pb(SCN)₂I₂ ($Pmn2_1$)¹⁴⁰, being potential materials exhibiting the effect. Rashba or spin splitting makes the 2D perovskites candidates for new applications, such as in spintronic devices.

Another interesting physical phenomenon observed in 2D perovskites is optical Stark effect, that is splitting of spectral lines in an external electric field. Spin-selective optical Stark effect has been demonstrated in thin films by means of transient optical

absorption spectroscopy. The phenomena can be potentially applied in quantum information⁶⁹.

3.6. Low temperature phases

The electronic and optical properties, discussed above, are highly correlative with the crystal structures of the two-dimensional perovskites. Applying high pressure or low temperature to the material is a direct way to affect its crystal structure and to observe the evolution of related physical properties. It may allow us to tune the structure in order to understand what leads to the improved properties and acts a guide for the design of new functionalities. Besides, searching structurally stable materials, that do not undergo any phase transitions, is important for practical applications under extreme conditions, for instance in space applications.

From this point of view, it is important to understand how the incorporation of the long organic cation affects compressibility and stability of the structure under changing temperature and pressure, and how this depends on nature of the cation and thickness of the inorganic layers (n).

Alkylammonium 2D perovskites were shown to crystalize in different phases below room temperature. For example $(C_{10}H_{21}NH_3)_2PbI_4$, one of the most studied 2D lead perovskites undergoes a structural phase transition at $\sim 270K$ ⁵⁸. The other members of $(C_mH_{2m+1}NH_3)_2PbI_4$ family also exhibit phase transitions, except for $m = 6$ ^{57,86,141}. The transition temperatures correlate the melting temperature of the corresponding amines^{33,142(p.308)}. Unusual optical behavior and phase transitions were reported for $(C_6H_{11}NH_3)_2PbI_4$ (derivative of cyclohexamine), resulting in additional PL peaks appearing at low temperature¹⁴³.

In contrast to the alkylammonium perovskites, materials containing benzene ring have not been found to undergo phase transitions at low temperature. For instance, $(PEA)_2SnI_4$ stays in the room temperature phase at least above 125 K¹⁴⁴. Low temperature properties of $(PEA)_2PbI_4$ have been reported extensively, and no phase transition was found in the range from 10 K to 340 K. However, inconsistency of the reported data should be emphasized. Thus Son-Tung Ha *et al.*⁷² reported a continuous

blue shift of the excitonic PL peak with cooling, while K. Gauthron *et al.*¹²⁴ and T. Ishihara³³ stated a red shift.

(PEA)₂(MA)Pb₂I₇ ($n = 2$) was reported to undergo a continuous blue shift excitonic and band edge energies while increasing temperature^{109,145}, but no detailed information and spectra were shown. Being an intermediate step between 2D and 3D perovskites, these unique materials require a more detailed analysis including their low temperature behavior.

Recently the 3D MAPbX₃ perovskites ($X = \text{I, Br, Cl}$) have been widely studied at various temperatures from the optical, structural, and vibrational points of view^{15,44,146}. In the range from 80 K to room temperature, the compounds were shown to undergo one to three structural phase transitions (depending on the halogen atoms) from orthorhombic to tetragonal phases, followed by a transition to a cubic (only for Cl and I) phase¹⁴⁷. The transitions are associated with the ordered and disordered state of the MA cation. In case of MAPbBr₃, MA cation is fully disordered in the cubic phase, while in the tetragonal hydrogen bonding between NH₃⁺ and Br⁻ freezes the rotation of MA (although the CH₃ end is free), resulting in lowering of symmetry and more distinct Raman MA modes. After the second phase transition, the rearrangement of hydrogen bonding takes place, making the MA totally ordered⁴²⁻⁴⁴. Besides, stability of the perovskites was reported to be related to hydrogen bonding¹⁴⁸.

According to current finding, the importance of hydrogen bonding in hybrid organic-inorganic perovskites should be considered. Experimental study of hydrogen bonding is a challenging target, because the main structural methods, such as XRD, do not always allow to find exact coordination of the light atoms such as hydrogen. On the other hand, Raman spectroscopy is sensitive to the formation of hydrogen bonds. Raman spectroscopy is a powerful tool to observe the structural changes, especially those involving the organic cations.

3.7. High Pressure Response

Due to very little high pressure works on 2D perovskites, to discuss the high-pressure response of layered perovskites it is necessary to discuss briefly the parent 3D hybrid perovskite structures.

MAPbBr₃ undergoes two phase transitions at very low pressure (< 2 GPa) and reversible gradual amorphization at 2-5 GPa¹⁴⁹. FAPbBr₃ is shown to be less compressible, undergoing two phase transitions at higher pressure and amorphization, starting above 4.1 GPa¹⁵⁰. MAPbI₃ undergoes two structural changes as well: 0.3 and 2.5 GPa, followed by gradual amorphization above 2.5 GPa^{151,152}. A pressure of 1 GPa that can be reached by chemical methods, is emphasized to be enough to improve the performance in solar cell application¹¹⁴.

All the described pressure-induced changes are fully reversible (with some hysteresis) for these materials, but some other effects stay permanent after decompression. A phase transition at 0.7 GPa followed by amorphization at 3 GPa was found in MASnI₃. Although no amorphization was observed during the second compression process up to 30 GPa. Thus, the structural stability was increased by applying high pressure. Besides, the electrical conductivity and photocurrent of the pressure-treated sample were improved as well¹⁵³.

Two competing processes take place under compression: *M-X* bond contraction, and tilting of the octahedra leading to change in the *M-X-M* angle (*M* is, for instance, Pb, X is halogen). It is interesting to note that all these materials first exhibit red shift in the band gap under compression that was explained by shrinkage of *MX*₆ octahedra and contraction of *M-X* bond in cubic or tetragonal phase resulting in stronger *M-X* interaction and hence decrease in the band gap. The tilting of the octahedra, exerting a stronger effect, leads to blue shift of the band gap in lower symmetry phases¹⁵⁰.

There have not been many publications on high-pressure study of layered perovskites by now. However, it is clear that high-pressure response of the layered perovskites is different from the phenomena described above for 3D perovskites. The compression of several members of 2D perovskites does not yield amorphization state in the range up to 30 GPa³⁵ nor leads to it at higher pressure in comparison with 3D perovskites; besides, the first structural changes normally occur under stronger compression too. For example, the first structural changes of octylammonium lead iodide happen at 12 GPa³⁴, and that of 2D copper(II)-chloride perovskite occurs at 4 GPa³⁵. Besides, although both 3D and 2D perovskites first exhibit red shift under compression, 3D perovskites then undergo blue shift, but 2D perovskites do not^{34,154}.

Thus, two-dimensional perovskites are less compressible and structurally more stable. The effect of different organic cation has not been studied in detail, and the high-pressure response of multi-dimensional perovskites ($n \geq 2$) is a point of interest due to their intermediate nature between 3D and 2D hybrid perovskites. Explanation of the gradual amorphization process in 3D perovskites was proposed to be related to methyl ammonium dynamics and hydrogen bonding¹⁵¹ that is to be confirmed.

3.8. Conclusions

2D perovskites have been repeatedly shown to be excellent candidates for application in optical devices. The unique properties and outstanding stability allow them to be used in solar cells, LED, spintronics, lasing, and so on. A clear understanding of the fundamental properties is critical for new 2D-perovskite based technologies. In this work, a review of the synthetic methods, physical, structural, and optical properties under various conditions is presented.

Different structural motifs have been discussed. The nature of organic cation has been demonstrated to significantly affect the crystal structure of the 2D perovskites. Thus, the research gaps regarding 2D perovskites are finding new organic molecules to form novel 2D structures, and deeper understanding of how the organic molecules and their states affects the materials under consideration.

Layered perovskites exhibit special properties, different from those of 3D perovskites. First of all, the natural quantum well structure gives stable excitons with high bonding energies, determining the optical properties even at room temperature. The excitons strongly interact with phonons, sometimes becoming self-trapped, and/or coupled with traps and spins, that makes 2D perovskites a very promising material system for novel functionalities and devices. Such phenomena as white light emission, Rashba band splitting, optical Stark effect have been demonstrated in particular members of layered perovskites and are to be studied more completely.

Besides the properties at ambient conditions, evolution of the properties at low temperature and under high pressure is a point of interest for providing a guide for synthesizing new materials and investigating structural stability. Although the temperature and pressure dependent optical and vibrational properties of 3D hybrid

perovskites have been studied in detail, our knowledge of 2D perovskites, especially of multi-dimensional hybrid Ruddlesden-Popper perovskites, is very limited. These materials act as intermediates between 2D and 3D perovskites that were found to exhibit different behavior under high pressure. Thus, evolution of the crystal structure and optical properties in these compounds under compression is of special interests.

Finally, improving crystallinity and vertical orientation in order to decrease charge recombination at grain boundaries and by other traps remain an important research topic since this plays a significant role for the device performance.

Chapter 4

Methyl Ammonium Dynamics and Optical properties in (PEA)₂(MA)[Pb₂I₇] Perovskite Dimorphs

4.1. Introduction

Organic cation dynamics and hydrogen bonding have been demonstrated to play an important role in the properties of 3D hybrid organic inorganic perovskites. For example, stability, phase transitions and band gap were reported to be related to hydrogen bonding¹⁴⁸. In case of MAPbBr₃, methylammonium dynamics (MA) cation is fully disordered in the cubic phase, while in the tetragonal hydrogen bonding between NH₃⁺ and Br⁻ freezes the rotation of MA (although the CH₃ end is free), resulting in lowering of symmetry and more distinct Raman MA modes. After the second phase transition, the rearrangement of hydrogen bonding takes place, making the MA totally ordered⁴²⁻⁴⁴.

(PEA)₂(MA)[Pb₂I₇] ($n = 2$, 2D perovskite) is intermediate to 3D MAPbI₃ and (PEA)₂[PbI₄] ($n = 1$, 2D) perovskites, containing MA cations, capable of forming hydrogen bonding. Ambiguity remains concerning the crystal structure and optical properties of this compound at low temperature (< 4.3 K)¹⁴⁵ nor has the influence of hydrogen bonding been studied. In this respect, Raman spectroscopy (RS) has proven a very sensitive probe for studying vibrations involving the hydrogen atoms in hybrid perovskites, especially MA molecule - halogen atom interactions in 3D perovskites⁴⁴.

This chapter describes low temperature RS investigations of N-H bond vibrations, particularly those related to the formation of N-H...I hydrogen bonds, to provide complementary information to single crystal X-ray diffraction where light elements are essentially invisible. Specifically, the absorption, emission and Raman vibrational modes of (PEA)₂(MA)[Pb₂I₇] in the temperature range 80 K - 293 K are analyzed. Correlating methyl ammonium cation vibrations and excitonic features revealed a phase transition happening in a wide range between ~150 and 200 K. NMR study revealed that the PEA cation is presented as two conformers, likely related to the water absorption. This phenomenon also contributes to disordering the material.

4.2. Results and Discussion

4.2.1. Structural characterization

Formation of the $n = 2$ (PEA)₂(MA)[Pb₂I₇] phase was confirmed by XRD analysis of the horizontally oriented platelets (Figure 4.1). The diffraction pattern, shown in Figure was indexed accordingly to the previous report¹³¹. All the peaks correspond to the (PEA)₂(MA)[Pb₂I₇] phase, no reflections from the $n = 1$ and $n = 3$ 2D perovskites were not observed.

Figure 4.1. XRD pattern of the horizontally oriented (PEA)₂(MA)[Pb₂I₇] platelets.

Besides, single-crystal X-ray diffraction was conducted in order to obtain the atomic coordinates. However, the crystals of the $n = 2$ perovskite (PEA)₂(MA)[Pb₂I₇], large enough for single crystal X-Ray diffraction, appeared to be irregular on a macroscopic scale, likely due to self-exfoliation. That does not affect optical and Raman studies since a confocal microscope was used for the measurements of small crystals with laser spot of micrometer size. Only coordinates of heavy inorganic atoms at room temperature could be obtained by means of single crystal X-ray diffraction, confirming the $n = 2$ layered structure as well. Uncertainty of the organic sublattice may be also related to disorder of MA and/or PEA cations, that is discussed below.

NMR study (presented in Figure 4.2) confirms a PEA⁺:MA⁺ cation ratio of ~2:1 which is consistent with the nominal (PEA)₂(MA)[Pb₂I₇] compositional stoichiometry.

Furthermore, the highly shielded (upfield) shift suggests that these H₂O position(s) (component 8 in Figure 4.2a) that are distant from the PEA⁺ or MA⁺ amine functionalities and the PbI surface, thus avoiding H-bonding arrangements that would introduce a deshielded (downfield) ¹H chemical shift. Given the well-known propensity for 2D perovskites to absorb H₂O^{2,3}, the most likely access is provided by the inter-

Figure 4.2. 1D solid state NMR data from the PEA₂MAPb₂I₇ system showing the (a) ¹H MAS NMR spectrum, deconvolution and assignments acquired under high-field/ultra-fast MAS conditions ($\nu_{0,1H} = 800.16$ MHz, $\nu_r = 110$ kHz).

planar region accommodating the PEA⁺ cations in the 2D ($n=2$) (PEA)₂(MA)[Pb₂I₇] system. Furthermore, the highly shielded ¹H shift suggests that the H₂O resides in the middle of the inter-planar spacing between the aromatic rings of the PEA⁺ cations.

The assignment of the MNR spectrum components is shown in Figure 4.2. The peaks associated with the α -CH₂ (H position 5) and β -CH₂ (H position 6) clearly split into at least two well-defined H chemical environments. It is accounted for the positional disorder characterizing the ethylamine side chain distributes the ¹H intensity from the α -CH₂ moiety between H positions 5 and 5'; similarly, the ¹H intensity from the β -CH₂ moiety is distributed between the H positions 6 and 6'. The disorder is likely due to two different PEA structural conformers proposed in Figure 4.2. These conformers differ markedly in the proximity of the amine functionality with respect to

the aromatic ring; PEA conformer **1** positions the amine functionality at a maximum distance away from the aromatic ring, while PEA conformer **2** suggests that the aliphatic side-chain and amine moiety wrap back towards the aromatic ring introducing much closer contact. This phenomenon, its relation to the water content and temperature dependence are to be studied in the future.

Figure 4.3. Differential scanning calorimetry (DSC) curves showing the gradual phase change in the temperature range from ~200 to 150 K. The shape of the curve suggests the 2nd order phase transition.

Differential scanning calorimetry DSC (Figure 4.3), measured between 140 and 270, revealed a gradual, very broad, second-order phase transition occurring in the range ~150-200 K. Further we correlate it with changes in optical properties and states of the organic sublattice.

4.2.2. Optical Properties

Exfoliated $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ sample exhibits strong excitonic photoluminescence and distinct absorbance at room temperature due to intrinsic crystallographic quantum confinement (Figure 4.4a,b)^{33,91}. For the present investigations, materials without the defect-trapped exciton emission peak were chosen and analyzed to extract the excitonic energy. Although the photoluminescence (PL) peaks were asymmetric pseudo-Voigt fitting took into account both homogeneous and

inhomogeneous broadening¹⁵⁵. The evolution of the excitonic absorption edge was monitored by applying a linear fit to the lower energy slope of the optical absorbance (OA) spectra.

Above 200 K, neither PL nor OA spectra show significant or sudden changes in intensity or frequency during cooling, aside from the gradual narrowing in full width at half maximum (FWHM) due to phonon population depletion. The excitonic absorption energy is almost unchanged during cooling from room temperature before a distinct blueshift of ~5 meV below 200 K returning to continuous redshift below 150 K (Figures 4.4c). An earlier study of (PEA)₂(MA)[Pb₂I₇] reported a small continuous red shift in absorption between 10 K – 293 K^{109,145} with absorption peak asymmetry providing inconclusive evidence of a phase transition. The integrated PL intensity (Figure 4.4d) generally increases during cooling with a discontinuity at ~200 K appearing concomitantly with the excitonic anomaly. The changes are reproducible, and a similar evolution of the optical properties was observed under decreasing (as in Figure 4.4) and increasing temperature. Together with the SDC results, the spectroscopy provides compelling evidence of a phase transition in the range 150-200 K.

Figure 4.4. Photoluminescence (PL, 457 nm excitation) and optical absorbance (OA) of (PEA)₂(MA)Pb₂I₇ at various temperature. a) Normalized PL and OA evolution under decreasing temperature; b) PL at different temperatures; c) Plot of PL peak position and excitonic absorbance edge energy versus temperature. d) Plot of dependence of integrated PL intensity in logarithmic scale on reversed temperature and fit by formula 1. e) Plot of dependence of excitation intensity integrated PL intensity on excitation laser power (bilogarithmic) at room temperature (pink plot) and at 80 K (green) and linear fit. The slope represents the power coefficient of the dependence and reflects the recombination mechanism.

Photoluminescence decreases with heating due to thermal quenching^{21,116} whereby the integrated PL intensity conforms^{115,124}

$$I = \frac{I_0}{1 + \alpha e^{\left(\frac{-E_a}{kT}\right)}}, \quad (4.1)$$

where I_0 is PL intensity at 0 K, E_a is the activation energy and α is a ratio of radiative and nonradiative lifetime at 0 K, representing contribution of the nonradiative process. The fitting of logarithmic integrated PL intensity vs inverse temperature is shown in Figure 4d. The activation energy (250(40) meV) for the room temperature phase was much larger than for the low temperature polymorph (125(10) meV). The latter energy is smaller than reported exciton binding energy value of 170 meV¹⁰⁹. This result, together with the significant reduction in PL intensity at 200 K, suggests transformation into the low temperature phase introduces additional defects and non-radiative pathways¹²⁴.

PL intensity is proportional to excitation intensity with a power law coefficient k , $I(PL) \sim P^k$, where the coefficient $k = 1$ describes the monomolecular free exciton recombination, $k = 1.5$ is for trapped exciton recombination, and to $k = 2$ for bimolecular free carrier recombination^{132,133}. Therefore, defect-related recombination pathways can be examined using excitation intensity dependent experiments. Figure 4.4e shows the log-log graphs of integrated PL intensity of (PEA)₂(MA)[Pb₂I₇] with excitation power. The slope of 1.5 at room temperature is consistent with the hypothesis of trapped states, and the slope of 1 at low temperature suggests the monomolecular free exciton recombination and an absence of other recombination passways^{132,133}. However, it is noted that traps (i.e. defects) may not be activated at 80 K.

4.2.3. Methylammonium dynamics

To investigate the structural evolution, temperature dependent Raman spectroscopy of (PEA)₂(MA)[Pb₂I₇] was conducted (Figures 4.5a, 4.6). The high wave number bands can be attributed to PEA and MA molecular vibrations with lower wavenumbers arising from the inorganic sublattice as reported for MAPbBr₃ and MAPbI₃^{15,44}. This interpretation was confirmed by comparing the Raman spectra of (PEA)₂[PbI₄] and (PEA)₂(MA)[Pb₂I₇] that allows the unambiguous assignment of methylammonium bands (910 (ρ MA), 970 (ν C-N), 1247 (ρ MA), 1478 cm⁻¹ (δ NH₃))

Figure 4.5. a) High wave-number Raman spectra of $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ at various temperature. MA modes are highlighted. Red points indicate the transition temperature. b) MA vibrational modes assignment.

with the balance contributed by phenylethylammonium. The vibration modes are illustrated in Figure 4.5b. Neither the PEA nor ν C-N MA bands split or change intensity in contrast to the NH_3 vibrations (Figure 4.5b). The relative intensity of the 910 cm^{-1} (ρ MA) band increases continuously below $\sim 200\text{ K}$, while those at 1247 cm^{-1} (ρ MA) and 1478 cm^{-1} (δ NH_3) become increasingly evident below $\sim 200\text{ K}$ (Figure 4.5). It is notable that C-N bond stretching frequency and intensity do not undergo any changes, confirming that only one rather than the both ends of the MA cation ends are involved in the transition. Thus, spectral changes involve vibrations contributed by the NH_3 ends bonding or rocking, showing that the transition is highly related to state of NH_3 and its hydrogen bonding.

Further evidence of a low temperature dimorph of $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ is found by low wave number Raman spectroscopy (Figure 4.6). It is notable that distinct bands persist even at room temperature below $< 150\text{ cm}^{-1}$ as the PEA molecules are relatively static, in contrast to 3D perovskites that exhibit only broad Raman bands due to dynamic MA/FA disorder,^{15,44,150} whereas PEA molecules render the inorganic sublattice more rigid with distinct low-wavenumber Raman bands. The peaks below $\sim 30\text{ cm}^{-1}$ can be attributed to PbI_6 tilting, those below 80 cm^{-1} to I-Pb-I bending; and

the peaks between 80 cm^{-1} and 150 cm^{-1} likely arise from Pb-I stretching. Bands <50 cm^{-1} cannot be assigned unique Raman modes.

Figure 4.6. Ultra-low wave-number Raman spectra of $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ at various temperature.

Nevertheless, temperature-dependent features are evident. For instance, the feature at ~ 30 cm^{-1} is distinct only after cooling, while the mode at 100 cm^{-1} , assigned to Pb-I stretching in the PbI_6 octahedron, splits, likely caused by octahedra distortion and/or the better resolved peaks due to more ordered rigid¹⁵⁶ structure, supported by hydrogen bonds at low temperature. These features in the temperature dependent spectra indirectly indicate uncontinuous evolution of crystal structure around 200 K, consistent with the other evidences of the phase transition.

The spectroscopic results consistently show a phase change starting at 200 K, highly related to methylammonium dynamics and its hydrogen bonding state. We found impossible to evaluate hydrogen-bonding length based on crystal structures, obtained by single crystal X-ray diffraction, neither published before⁶¹ nor our own results. None of the attempts yielded exact coordinates of the MA cations, probably due to partial disorder at room temperature, while DFT relaxation provides orientation and partial atomic coordinates of MA without considering thermal energy and

disordering. The detailed analysis of the possible configurations of the MA cation based on DFT calculations will be reported elsewhere.

As shown in Figure 4.7, the octahedral tilting causes a reduction in the I-Pb-I angle to 155° (according to our single crystal X-Ray diffraction results), which is a substantial distortion from 179° for MAPbI₃ structure at room temperature¹⁵⁷. This octahedral tilt distorts the bond lengths, bond angles and, most importantly, shape of the cuboctahedral cavity accommodating the MA⁺ cation. In this case the degrees of freedom available for the MA⁺ cation motion become restricted, thus resulting in altered MA dynamics in comparison to MAPbI₃¹⁵⁷. The MA⁺ cation dynamics in MAPbI₃ at room temperature has been shown to undergo ultra-fast reorientation using quasi elastic neutron scattering, GHz spectroscopy, ¹⁴N NMR and electron diffraction, with the resulting reorientation time (τ_{rot}) residing in the picosecond^{158–160}. The MA reorientation dynamics in MAPbI₃ have also been investigated using ¹H T_1 (spin-lattice) relaxation experiments,^{157,159,161,162} with Kubicki *et al.* reporting the ¹H T_1 of the CH₃ and NH₃⁺ moieties to be ~16 s when measured at 21.1 T (900 MHz)¹⁶².

Figure 4.7. Representations of the inorganic sublattices in 3D¹¹ and 2D perovskites.

The MA reorientation dynamics in MAPbI₃ have also been investigated using ¹H T_1 (spin-lattice) relaxation experiments. In the present study, similar ¹H T_1 measurements were undertaken on PEA₂MAPb₂I₇ at 18.8 T and the results summarized in Figure 4.8 show that much shorter T_1 s characterize both the MA⁺ and PEA⁺ cation dynamics in this system. As demonstrated in Figure 4.8, the saturation-recovery T_1 data has been fitted with single exponential functions and all the measured ¹H T_1 values fall within a narrow range of ~2.4 - 3.1 s. In particular, the ¹H T_1 relaxation of the CH₃ and NH₃⁺ groups (3.1 and 2.8 s, respectively) comprising the MA⁺ cation in

PEA₂MAPb₂I₇ indicate significantly slower reorientation processes in comparison to those encountered in the MAPbI₃ system, which are consistent with the more hindered and slower modes of MA⁺ cation motion induced by the smaller and distorted cuboctahedra cavities in the PbI framework.

Figure 4.8. ¹H T₁ data from the MA⁺ CH₃ (red) and NH₃⁺ (black) proton species, and the PEA⁺ NH₃⁺ (blue) proton species, measured with the saturation-recovery technique.

However, Raman spectroscopy gives solid proof of the changes, involving vibrations of the NH₃ end of the MA cation with temperature decrease. These spectral changes arise from MA ordering through hydrogen bonding that promotes harmonic vibrations and more rigid structure yielding more intense and narrower bands as noted elsewhere for the 3D perovskites MAPbX₃ (X = Br, I)^{15,44,163}. Therefore, the MA cation in the *n* = 2 perovskite is less free than completely disordered MA in cubic 3D MAPbI₃. It is interesting, that in MA in the *n* = 2 perovskites strengthening hydrogen bonding at higher temperature 200 K than the 3D counterparts: the hydrogen bonding appears at 162 K in MAPbI₃ and at 144 K in MAPbBr₃ during the order-disorder transition¹⁶³ with the hydrogen bond energy evaluated as 0.09 eV per bond. Moreover, hydrogen bonds form gradually in contrast with 3D perovskites, and the changes in excitonic energy (5 meV in 2D vs 80 meV in 3D) and crystal structure of the inorganic sublattice (according to Raman spectroscopy) are not as significant as in MAPbI₃ during the phase transition. The main difference between the 3D perovskites and the one under consideration is the presence of the long organic PEA cations. Thereby, the interlayer big organic molecules stabilize the entire structure: disruption of the hydrogen bond interactions due to thermally activated disorder completes at higher temperature in

presence of PEA, and the structure at room temperature is not as disordered as the 3D counterpart is.

4.3. Conclusions

It has been demonstrated in the 2D hybrid perovskite that (PEA)₂(MA)Pb₂I₇ undergoes a crystallographic transition in the range ~200-150 K driven by the formation of hydrogen bonds. Although in comparison with MAPbI₃, MA cation is confined even at room temperature phase, decreasing temperature causes strengthening of the hydrogen bonding. This process happens in the wide temperature range, causing a gradual phase transition. Thus, the importance of methylammonium dynamics on structural and optical properties was emphasized for 2D perovskites. It is interesting to note that the PL intensity in the LT phase has a linear dependence on the excitation laser power, indicating that the LT phase has excellent luminescence properties. However, the recombination pathways in the material in both phases are a subject for further study.

4.4. Methods and Materials

Synthesis The synthesis procedure described previously by Stoumpos et. al.⁸⁰ was used to obtain crystalline (PEA)₂(MA)Pb₂I₇, however, the method was modified to include excess of methyl ammonium iodide. Inorganic lead iodide (99.999%, trace metals basis, perovskite grade), phenyl ethyl amine (99%), 57% w/w non-stabilized aqueous HI solution, and 50% aqueous H₃PO₂ were obtained from Sigma Aldrich, while methyl ammonium iodide was purchased from Dye Sol. These reagents were used without purification unless otherwise stated in the associated procedure.

Preparation of PEAI. Phenyl ethyl ammonium iodide was prepared by slowly mixing the amine with a stoichiometric amount of hydrochloric iodide in ethanol at 0 °C for 1 hour, after which the solvents were removed by rotary vacuum evaporation at 50 °C. Where necessary, excess ethanol was added to form an azeotropic mixture with water to remove the latter completely. The solid product was washed with diethyl ether to remove the remaining iodines. Finally, the ammonium salt was dried under vacuum at 50 °C overnight (1.76g; 83% yield). ¹H NMR (400 MHz, DMSO-d₆): δ 7.78 (bs, 3 H, NH₃), 7.32-7.20 (m, 5 H, ArH), 3.06-3.03 (m, 2 H, CH₂), 2.88-2.84 (m, 2 H, CH₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 137.1, 128.6, 128.6, 126.7, 40.0, 32.8.

$(\text{PEA})_2(\text{MA})\text{Pb}_2\text{I}_7$ ($n = 2$). A two-necked round bottom flask was used to combine PbI_2 powder (230 mg, 0.5 mmol), methyl ammonium (53 mg, 0.33 mmol) and phenyl ethyl ammonium iodide salts (125 mg, 0.5 mmol) with magnetic stirring. Methyl ammonium iodide was added with 30% excess. Subsequently, 57% w/w aqueous HI solution (2.0 mL mL) and 50% aqueous H_3PO_2 (0.20 mL) were added dropwise(?) sequentially. The suspension was brought to reflux under flowing N_2 with continuous stirring (30 - 60 mins) to yield a clear bright yellow solution. Stirring was discontinued and the solution cooled slowly to room temperature while red rectangular plates precipitate. The crystals were finally isolated by vacuum filtration, washed with copious amounts of diethyl ether, and thoroughly dried under vacuum for several hours.

Multinuclear Solid State ^{13}C and ^1H MAS NMR. All solid-state MAS NMR measurements were acquired at 18.8 T using a Bruker Avance III-800 spectrometer operating at ^1H and ^{13}C Larmor frequencies of 800.16 and 201.19 MHz, respectively. These measurements were undertaken using a Bruker 0.7 mm triple channel H/C/N ultrafast MAS probe which enabled a MAS frequency of 110 kHz throughout this study. The ^1H MAS NMR data were acquired using single pulse methods which utilised a $\pi/2$ pulse length of 1.0 μs (calibrated using adamantane) and a recycle delay of 30 s. In contrast, the ^1H - ^{13}C cross-polarisation (CP)MAS NMR data were measured using an initial ^1H $\pi/2$ pulse time of 1.0 μs , a Hartmann-Hahn contact period (in the form of a CP ramp) of 2 ms, in conjunction with ^1H decoupling fields of >100 kHz during data acquisition. Both ^1H and ^{13}C chemical shifts were both referenced against TMS as the primary IUPAC reference ($\delta_{\text{iso}} = 0.0$ ppm) via a secondary solid adamantane reference ($\delta_{\text{iso}} = 1.9$ ppm for ^1H ; $\delta_{\text{iso}} = 37.7$ ppm for ^{13}C). The ^1H MAS NMR data were accurately simulated using the DMFit NMR software package to quantitatively estimate the relative proportions of the individual PEA^+ and MA^+ cations present.

Two-dimensional heteronuclear ^1H - ^{13}C correlation data was achieved through the use of the inversely detected hCH HETCOR experiment utilising forward ^{13}C - ^1H CP, evolution of the ^{13}C magnetisation under fast MAS and high ^1H decoupling conditions, and then reverse ^{13}C - ^1H CP for detection of the ^1H magnetisation. The preparatory ^1H and ^{13}C $\pi/2$ pulse lengths prior to the forward and reverse CP processes

were both 1 μ s in duration, while the forward and reverse CP ramps (contact periods) were both 2 ms. The 2D homonuclear ^1H - ^1H NOESY data were acquired using mixing times of 100 and 300 ms, a recycle delay of 5 s, with each experiment acquiring 160 slices in the indirect F1 dimension. The 2D homonuclear ^1H - ^1H single quantum-double quantum BABA recoupling experiment was performed using a single rotor synchronised recoupling loop of 9.1 μ s, a double quantum evolution period of 15 μ s, with 1280 slices comprising the indirect F1 dimension. All data were processed using the Bruker TopSpin (v 4.0.8) NMR data processing package. The ^1H T_1 relaxation times were measured using a saturation-recovery experiment. An initial pulse train of 100 $\pi/2$ pulses with a separation delay of 50 ms was used to achieve complete saturation prior to single pulse acquisition. The resulting data were deconvoluted and integrated using Dmfit simulation program.¹ The resulting integrated intensity data from each ^1H resonance was fitted with a single exponential function using OriginPro (2019) software to obtain the ^1H T_1 (spin-lattice) relaxation times.

Optical characterization A WITec Alpha 300RAS confocal Raman microscope was used to record Raman, photoluminescence (PL) and optical absorption spectra. The 633 nm (red) line from an 8 mW He–Ne gas laser was chosen to avoid photoluminescence. To achieve a suitable signal quality, each low wave-number Raman signal was collected for 10 s, and high wave number – for at least 50 s. The Raman signal was coupled to an Acton spectrometer with a diffraction grating of 1800 grooves/mm (1.3 cm^{-1} resolution) and a thermo-electrically cooled Andor CCD detector. The backscattered Raman signal passed through two 633 nm BragGrate Notch Filters (BNF) for effective laser line rejection.

The blue line of a linearly polarized CW solid laser (457 nm) was chosen for PL measurements with the excitation power maintained below 0.8 μ W to avoid detector photo degradation and saturation, with the integration time of 1 s. A halogen lamp (15 V, 150 W, 3100 K) served as the white light source for the absorption measurements. A long working distance 20 $\times$ microscope objective (Nikon NA0.35, WD24mm, spot size of ~ 2 μ m) was used. Spectra were collected between 293 K and 78 K using a Linkam stage (see Chapter 2.2.2 for more details).

XRD and Single Crystal X-ray Diffraction. Shimadzu XRD-600040 diffractometer in θ - 2θ scan mode with the measurement rate of 1 degree/min was used

to record the XRD pattern at room temperature. Cu-K α (1.5406 Å) X-ray line was chosen as a source, using scintillation NaI detection. The pattern was collected from a polycrystalline sample in a form of many horizontally oriented platelets. Origin Pro software was used to fit the experimental points. Single crystal X-ray diffractions were accumulated with a CCD detector (Bruker X8 CCD diffractometer) at room temperature using a graphite-monochromated Mo-K α source ($\lambda = 0.71073$ Å). Data reduction and absorption corrections were performed with SAINT and SADABS respectively. The motif of the inorganic sublattice was determined by direct methods using the Bruker SHELXTL-2014 package. The location of the organic moieties (MA and PEA) were not be determined.

Chapter 5

Strong Optical, Electrical and Raman in-Plane Anisotropy in Corrugated Two-Dimensional Perovskite

5.1. Introduction

The focus of this chapter is 2D halide perovskites formed by corner sharing $M-X$ octahedral layers, sandwiched by the moderately-sized A cations. Vast majority of these materials consist of flat inorganic sheets, which can be abstractly derived from the $\langle 100 \rangle$ crystallographic planes of the parent cubic 3D inorganic lattice (Figure 5.1a). A smaller subset of 2D perovskites contain corrugated inorganic layers, similarly derived from the $\langle 110 \rangle$ or $\langle 111 \rangle$ crystallographic planes^{25,37,81,90}. In comparison to the $\langle 100 \rangle$ counterparts, the instances of the so called corrugated 2D perovskites are rarer due to the more specific templating requirement of the structure^{81,164}. The limited examples include (EDBE)[PbBr₄] (EDBE = 2,2-(ethylenedioxy)bis-(ethylammonium))⁴⁰ and (ImEA)[PbI₄] (ImEA = imidazolium ethylammonium)¹⁶⁵ whose inorganic lattices feature $\langle 110 \rangle$ -oriented perovskite sheets (Figure 5.1b).

Figure 5.1. Crystal structures Schematic diagrams of a) 3D and 2D hybrid perovskites. Crystal structures of b) corrugated $\langle 110 \rangle$ 3×3 2D perovskite (ImEA)[PbI₄] and c) black phosphorus – a well-known in-plane anisotropic material.

Having well defined “armchair” and “zigzag” directions, the structural motif of the aforementioned corrugated 2D perovskites is similar to that of black ^{166–168} (Figure 5.1c), a material well known for its in-plane anisotropic properties. As such, in addition to the strong intrinsic anisotropy between in-plane and out-of-plane directions, the corrugated perovskites is also expected to exhibit in-plane anisotropy. However, despite the extensive reports on their synthesis, characterization, and applications, the in-plane anisotropic properties has never been observed in 2D perovskites. In contrary, in-plane anisotropy has been observed in a few 2D materials^{169,170}, such as black phosphorus^{166–168} and low-symmetry transition metal dichalcogenides (TMD)^{171,172}. These in-plane anisotropic materials demonstrate unique physics: anisotropic plasmons¹⁷³ and electron-phonon interactions¹⁷⁴, and linear dichroism¹⁷⁵. Besides, some

anisotropic 2D materials, such as black phosphorous^{174,176} and other TMDs^{177,178} have been reported to exhibit anisotropic electron-photon and electron-phonon interactions through angle and excitation wavelength dependent resonant Raman response, but its effect on photoluminescence has not been demonstrated before this work. More importantly, 2D materials usually form well-oriented films and platelets. For example, bulk crystals of 2D perovskites are known to exhibit thickness (out-of-plane) of tens and hundreds times less than the in-plane dimension. Hence, existence of such additional degree of freedom makes the materials perfect candidates for novel optoelectronic and electronic devices: polarisation detectors¹⁶⁸, polarizers and plasmonic devices¹⁶⁶, etc¹⁶⁹.

Herein, we report, for the first time, in-plane anisotropy behaviour in single crystals of 2D perovskite (ImEA)[PbI₄]. The in-plane anisotropy was demonstrated firstly by angle-dependent Raman spectroscopy with non-polarized detection as well as in parallel or cross-polarization configurations. This method can be further utilised for instant determination of the single crystal orientation. From the polarization-resolved angle-dependent reflectance spectroscopy, we observe three types of excitons with energies about 2.54, 2.56 and 2.67 eV having different responses to the polarized light. First-principles band structure calculations suggest free charge transitions, corresponding to these excitons¹², which could explain the anisotropy observed. An abnormal photoluminescence (PL) response was found under angle-resolved linearly polarized excitation. Depending on the angle between polarisation of the excitation laser and the crystallographic axis, the PL peak energy was continuously changed by ~20 meV at room temperature between the two in-plane orientations. Temperature dependent PL analysis under polarized excitation implies different exciton-phonon interaction strength and deformation potentials along *b* and *c* directions of the crystal. Finally, in-plane photoconductivity anisotropy is also demonstrated in (ImEA)[PbI₄].

5.2. Results and Discussion

5.2.1. Raman anisotropy

Raman spectroscopy is a powerful tool for studying the vibrations and structure of anisotropic materials and can be used to determine the crystal orientation. The Raman spectrum of (ImEA)[PbI₄], as well as that of other low-dimensional hybrid

organic-inorganic perovskites¹⁵⁶, contains a variety of vibrational modes, many of which overlap with each other (Figure 5.2). The modes with frequencies above ~150 cm⁻¹ originate from vibrations of the organic molecules, while the modes below 150 cm⁻¹ are mainly contributed by vibrations of the inorganic sublattice^{15,165}. The low-wavenumber vibrations can be separated into two groups: below ~70 cm⁻¹, attributed to the PbI₆ octahedral bending, while the rest correspond to the symmetrical and asymmetrical stretching of Pb-I bonds^{156,165,179}.

A symmetry-based analysis of the angle dependence of the Raman spectra was performed. According to Bilbao Crystallographic Server, space group *P2₁/c* corresponds to C_{2h} (2/m) point group; the vibrations belong to one of four types: A_g, A_u, B_g, or B_u, where only A_g and B_g are Raman active⁴⁸:

$$\widetilde{R}(A_g) = \begin{vmatrix} a & 0 & d \\ 0 & c & 0 \\ d & 0 & b \end{vmatrix}, \quad (5.1)$$

$$\widetilde{R}(B_g) = \begin{vmatrix} 0 & e & 0 \\ e & 0 & f \\ 0 & f & 0 \end{vmatrix}, \quad (5.2)$$

The polarization of both the incident and scattered light are set as

$$e_i = (0, \cos \theta, \sin \theta), \quad (5.3)$$

$$e_{s\parallel} = (0, \cos \theta, \sin \theta), \quad (5.4)$$

$$e_{s\perp} = (0, -\sin \theta, \cos \theta), \quad (5.5)$$

θ is the angle between axis *c* and the polarization of the incident laser. Based on the equations 2.3, 2.4 and the equations 5.1-5.5, given above, one can derive theoretical equations for the angle dependence of A_g and B_g intensities in various geometries of the experiment. The resulting equations (5.6-5.11) are summarized in table 5.1.

Due to the complexity of the crystal structure and a great number of the inorganic Raman modes, even the resolved Raman peaks are likely to be a superposition of separate Raman modes, being contributed by both A_g and B_g modes. We applied the equations to fit the angular behaviour of the main peaks intensities (heights) and both of them yielded good fit. Fits by equations 5.6-5.11 are shown in Figure 5.2 c, e-h as solid lines. Similar analysis of the angle resolved spectra, collected in parallel and cross configurations is provided in supporting information. The peaks at 7, 31 and 41 cm⁻¹ are better described in A_g symmetry, as well as the organic

vibrations in the range 300-610 cm⁻¹, while the angular behaviour of the peaks at 17 and 110 cm⁻¹ demonstrated that they stem from the contribution of both A_g and B_g symmetries.

Table 5.1. Analytical equations of the angle dependence of the A_g and B_g modes intensities in various geometries of the experiment. The laser propagation and detection direction is normal to the *bc* plane (in-plane), θ is the angle between axis *c* and polarization of the incident laser.

Geometry of the experiment	I(A _g)	I(B _g)
Non- polarized detection	$I_{(Ag)} = c^2 \cos^2 \theta + (b^2 + d^2) \sin^2 \theta$ (5.6)	$I_{(Bg)} = f^2 + e^2 \cos^2 \theta$ (5.7)
Parallel polarized	$I_{\parallel(Ag)} = (c \cos^2 \theta + b \sin^2 \theta)^2$ (5.8)	$I_{\parallel(Bg)} = f^2 \sin^2(2\theta)$ (5.9)
Cross- polarized	$I_{\perp(Ag)} = \left(\frac{b}{2} - \frac{c}{2}\right) \sin 2\theta$ (5.10)	$I_{\perp(Bg)} = f^2 \cos^2 2\theta$ (5.11)

We used single crystal X-ray diffraction to determine the orientation of the crystals, and to assign the (*hkl*) values to the faces of the crystals and hence the direction of monoclinic unit cell vectors *a*, *b* and *c*. These unit cell vectors were corroborated through Raman spectra (Figure 5.2a), as most of the Raman peaks reach maximum intensities when the excitation laser polarization is along the *c*-axis of the crystal (Figure 5.2c). Raman spectra with *non*-polarization-specific detection are very useful for instant determination of the crystal orientation, and the use of intensity ratio of the particular peaks is more convenient (Figure 5.2d).

Figure 5.2. a) Angle-resolved Raman spectra (633 nm excitation) of (ImEA)[PbI₄] with non polarization-specific detection configuration. b) Geometry of the experiment: laser propagation direction is normal to the *bc* plane of the crystal. During the experiment, the angle between the sample and the polarization direction of the laser was rotated. c) Polar plots of the chosen mode intensities (heights) and d) polar plots of the ratios of the chosen mode intensity, proposed to be used for the crystal orientation determination. e-h) Polar plots of intensities of the particular Raman peaks, collected in parallel (e, g) and cross (f, h) configurations; (e) and (f) correspond to the inorganic vibrations, and every peak is likely to be contributed by several vibrations that are not resolved; (g) and (h) represent some of the vibrations of the organic counterpart. Experimental points were fit by equations 5.6-5.11.

5.2.2. Optical anisotropy

Reflectance. Anisotropic optical response of the single crystal sample was first probed by polarization-resolved reflectance spectroscopy, by varying the angle between the incident light polarization and in-plane axes of the crystal. The corresponding reflectivity spectra were plotted as $R = \frac{R_{\text{sample}}}{R_{\text{substrate}}}$ and shown in Figure 5.3a. The reflectivity spectra are notably polarization-dependent.

As discussed in Chapter 2.1.2, the real and imaginary part of the dielectric function (and the refractive index) are not independent parameters, the relation can be expressed by Kramers-Kronig (KK) relationship⁵². Thus, KK analysis of reflectivity spectra allows to obtain the absorption coefficient. In practice it is not a trivial task, particularly the precise KK analysis requires a reflectivity data recorded at a wide frequency range. In our case the KK relationship was applied to the data between 1.7 eV and 3.2 eV, while the excitonic features of interest take place in the relatively

Figure 5.3. a) Angle-resolved reflectivity spectra recorded at 80 K; b) angle-resolved absorption coefficient, calculated from reflectivity spectra with use of Kramers–Kronig relations^{52,53}; c) optical absorption spectra of bulk (ImEA)[PbI₄] from G_0W_0 +BSE calculations with considering spin-orbital coupling effects for incident light polarized along b (blue line) and c (red line) direction. d) and e) calculated real-space exciton wavefunctions corresponding to the main E_1 peak at ~ 2.4 eV (d) and E_3 at ~ 2.5 eV (e). The hole position is fixed close to a Pb atom (red sphere) and the resulting electron distribution is displayed. The plot size corresponds to a $2 \times 2 \times 2$ unit cell.

narrow region from 2.5 eV to 2.7 eV, so the accuracy is satisfactory for at least qualitative comparison of the dielectric functions. Several models have been proposed to fit the reflectivity spectra. Here we apply the method of the KK-constrained variational fitting, proposed by Kuzmenko⁵³, using the RefFIT software. The experimental points, recorded at 80 K, (large empty dots) of the reflectivity spectra were fitted (solid lines) by the Kramers-Kroing (KK)-constrained variational method for different relative orientations of the crystal and polarization of the insistent light, as shown in Figure 5.3a.

The corresponding absorption coefficient functions are plotted in Figure 5.3b. Notably, the absorbance with three excitonic resonances (E_1 , E_2 and E_3) are also anisotropic. The intensity of three exciton peaks are angle-dependent: E_1 reaches its maximum under excitation along c axis and continuously decreases from 90° (c axis) to 0° (b axis). E_3 shows a similar tendency and even disappears while excited along b axis. The evolution of should peak E_2 is more complex, its contribution reaches the maximum at $\sim 30\text{-}45^\circ$ from b axis.

To gain more information on the anisotropic nature of the low-lying excitonic transitions, we performed GW-BSE-based *ab initio* calculations for bulk (ImEA)[PbI₄] to compute the polarization-resolved absorption spectra for incident light polarized along b and c direction (Figure 5.3c). Our GW-BSE calculations successfully reproduced the anisotropic nature of the low-lying optically bright excitons. Along b axis, the first main peak is placed at ~ 2.40 eV, attributed to the excitonic transition E_1 from the valence band maximum (VBM) to the conduction band minimum (CBM) (see Supporting Information for details). The scenario changes along c axis: a new exciton peak is present at ~ 2.50 eV with ~ 100 meV higher than E_1 . The energy difference between these two low-lying excitons is in excellent agreement with the experimental absorption spectra in Figure 5.3b and thus the high-energy exciton should be assigned as E_3 . The intensity of E_1 also shows a marked dependence on the light polarization direction, which is consistent with our measurements. Figure 5.3d and 5.3e present the excitonic spatial wavefunctions distribution for E_1 and E_3 . Obviously, E_3 shows highly polarized dipole character along c axis, whereas E_1 is weakly polarized in the planes and distributed along the zigzag Pb-I chains, leading to a polarization-dependent intensity evolution along [010] and the [001] crystallographic directions

The performed GW-BSE calculations have not captured the nature of the shoulder component E_2 . Interestingly, it is separated from the component E_1 by ~ 30 -40 meV. A similar phenomenon has been repeatedly observed in $(\text{PEA})_2[\text{PbI}_4]$ 2D perovskite (PEA^+ is phenylethylammonium) both in the PL and absorption spectra, however the origin of the exciton fine structure has not been agreed, being attributed to the phononic sidebands¹⁸⁰, polaronic effects^{181–183}, Rashba effect¹⁸⁴, bi-excitons¹⁸⁵, and exciton-polarons related to the organic vibrations¹⁸⁶.

Photoluminescence. To our delight, angle resolved photoluminescence (PL) spectroscopy yielded unexpected results. Angle-resolved photoluminescence spectra (457 nm excitation) recorded at room temperature are shown in Figure 5.4. The experiment geometry was designed similarly to that of Raman spectroscopy measurement (see Figure 5.2b and experimental section for details), where excitation was caused by linearly polarised laser and recorded under several angles between the laser polarisation and in-plane crystallographic axes of the crystal. In contrast with only polarization-dependent PL intensity observed in anisotropic materials of different classes¹⁶⁹, $(\text{ImEA})[\text{PbI}_4]$ exhibits obvious energy shift of the PL peak by over 15 meV. A similar phenomenon has been reported in 2D perovskites – the PL energy anisotropy was observed between in-plane and out-of-plane directions^{187,188}. Peijun Guo explained the shift of PL energy by the anisotropic reabsorption effect due to the significant variation of the absorption coefficient. In the other work by Junze Li et al, this explanation was doubted and the energy variation was accounted for optical anisotropy related to the quantum well-like structure.

We also noted that the absorption coefficient experiences a similar shift, and several components resolved at low temperature. Thus, the simplest explanation of the PL energy shift is co-existence of at least two overlapping components unresolved at room temperature, particularly E_1 and E_2 , identified in the reflectivity spectra. Close comparison of the PL and absorption peaks was conducted to check this hypothesis and is demonstrated in Figure 5.4 b. With the incident light polarization oriented along the b axis of the crystal (blue lines), PL and absorption peaks are symmetrical to each other with a little Stokes shift, the contribution of the E_2 component to α is negligible. The polarization oriented along the c axis yields red shifts of the PL and absorption peaks,

Figure 5.4. a) Angle-resolved photoluminescence spectra recorded at room temperature under 457 nm excitation, red spectra were collected with excitation along c axis, the blue one – along b axis, the rest – in between; all were measured with non-polarised signal collection. b) Comparison of normalized PL peaks (solid lines) with normalized absorption coefficient (dash lines), both obtained at 80 K, with various direction of the excitation polarization. Absorption coefficient was calculated from reflectivity spectra with use Kramers–Kronig relations. The arrows indicate the components.

but absorption undergoes significant broadening due to the contribution of E_2 . Notably, the component E_2 exhibits more complex dependence on angle – its contribution rises from the c axis (0°) to $30\text{--}45^\circ$ and then decreases to the b axis (90°) again. But the peak at 90° (b axis) is more blue shifted than at 30° , although the relative contribution of the component E_2 is lower. This demonstrates that the E_1 component undergoes a similar variation in energy as the PL peak, independently from the E_2 component. The state E_2 is not present in photoluminescence due to being either non-radiative or quickly relaxing to E_1 . The nature of the E_2 component is unclear at this time, but it is unlikely to contribute to the spectral anisotropy of the photoluminescence.

Figure 5.5. Simulated overlap of two PL peaks separated by 20 meV with FWHM equal to that obtained at 80K.

Besides, the scenario with two components does not explain why the separation between the two differently polarized PL peaks is noticeably temperature dependent (5.6a, b), increasing more than twice at higher temperatures. Finally, even if at room temperature the PL spectral anisotropy was caused by two components, they would be expected to resolve at lower temperature. The evolution of the PL spectra, shown in Figure 5.6a, demonstrates continuous sharpening of the peak with decreasing temperature. We simulated the scenario where PL was a superposition of two peaks separated by 20 meV with shape and full width at half maximum (FWHM) as taken from the experimental data at 80 K and found that the two components were resolved (Figure 5.5).

Asymmetry of the photoluminescence peak in hybrid perovskites is a typical phenomenon and has been explained by splitting the states due to electron-hole exchange interactions^{66,76}, or by phonon-related processes^{76,109,189}. Notably, the absorption peak is also asymmetric, but as a mirror image of PL, that implies interaction with phonons. The complex shape of the peaks did not allow performing reasonable fitting of the spectral line, thus we used parameters obtained from the experimental lines directly: energy of peak maximum, weight at half of the maximum height as FWHM, and integrated area under the line as intensity for further analysis. This approach is likely to cause a significant error in evaluating the constants, presented below, but allows a qualitative comparison of them.

We performed temperature dependent photoluminescence analysis, shown is Figure 5.6. Three points are noteworthy. First, the difference of photoluminescence energy along *b* and *c* axis reduces with temperature decrease, always remaining below thermal energy. Photoluminescence is more intense under excitation along *b* axis, but fitting with Arrhenius equation²¹

$$I = \frac{I_0}{1 + A e^{(-\frac{E_a}{kT})}}, \quad (5.14)$$

gives the same values of activation energy $E_a = 130(20)$ meV along the two in-plane directions (Figure 5.6c). I_0 represents PL intensity at 0 K, k is the Boltzman constant,

Figure 5.6. Evolution of photoluminescence of (ImEA)[PbI₄] and its parameters with temperature. Pink colour represents excitation along *c* axis, blue one – along *b* axis. a) normalised photoluminescence spectra vs temperature, excited by linearly polarised 457nm laser; b) plot of the energy of the photoluminescence peaks maximum; c) Arrhenius plot of integrated photoluminescence intensity. The dots represent experimental data, the lines are fitting by eq. 5.14; d) Full width at half maximum of the PL spectra vs temperature. The dots indicate experimental points, solid and dash lines – fitting by eq. 5.15.

T is temperature. The activation energy in this case may correspond to defect states or to exciton binding energy¹⁶⁵. Interestingly, the activation energy does not differ between the in-plane oriented excitons. Finally, the evolution of FWHM with temperature, shown in Figure 5.6d, differs for the two main directions. The difference is obvious at room temperature, and we applied exciton-phonon interactions theory^{123,124} to investigate the physical phenomenon.

Phonons can influence charges in a semiconductor in a few ways¹⁹⁰. First, the atom displacement caused by vibrations changes the electronic band structure – a phenomenon, called deformation potential. This provides the best approximation for the short-range interactions of charges and acoustic or optical phonons. Second, the carriers are affected through Coulomb force by the dynamic field created by LO phonon

vibrations in ionic crystals. This mechanism is called “Fröhlich interaction” and implies a long-range force and optical phonons. Although all the phonons can contribute to the interactions, the effects involving the longitudinal phonons are more dominant^{73,123,190}. Besides the phonons, charges can be scattered by impurities¹²³. These effects broaden emission line with temperature. There have been several models applied to describe dependence of photoluminescence peak width on temperature^{73,123,190,191}. To understand the anisotropy of FWHM and its changes following the temperature, the experimental FWHM values were fit by equation 3.2, based on the Fröhlich theory as discussed in chapter 3.5^{123,124}. Zhi Gou et al. proposed an alternative mechanism of the interactions: they showed that contribution of homopolar optical (HO) phonons through deformation potential is more significant than that of LO phonons in case of atomically thin 2D perovskites⁷³. However, population of HO phonon is following the same exponential law as of LO phonons (at high temperatures), so equation (3.2) is correct for this model.

In polar semiconductors, the effect of coupling with LO (or HO) phonons is much stronger than that with acoustic ones, and contribution of the latter is sometimes ignored^{73,123}. We neglected the contribution from the impurities and just considered the contribution of LOs, because the functional shape of the plot implies the strongest contribution from LO phonons¹²³. It should be noticed that the contribution from acoustic phonons was found to approach 0, similar to 3D perovskites¹²³. We applied the model to fit the experimental data, and fitting parameters are presented in table 5.2. The exciton-phonon coupling strength, as well as the phonon energies, differ significantly for the excitation along *b* and *c* axes, with the stronger interactions along axis *b*.

Table 5.2. Exciton-phonon coupling parameters, obtained by fitting of the FWHM(T) by eq. 5.15.

	Γ_0 , meV	γ_{LO} , meV	$\hbar\omega$, meV/cm ⁻¹	γ_{ac} , eV/K
Along <i>b</i>	27.6	300(20)	35(1)/280(10)	→0
Along <i>c</i>	27.6	190(30)	29(1)/230(10)	→0

The obtained values of γ_{LO} are similar to that in GaN, reported to be in the range from 165 to 525 meV¹⁹², but are an order of magnitude higher than in most of the reported hybrid perovskites. Electron-phonon interactions strength in 3D hybrid perovskites APbX₃ (A = MA or FA, X = I or Br) was reported in the range from 10 to 60 meV^{123,155}, whereas conventional 2D Ruddlesden–Popper perovskite phenylethylammonium^{181,193} and alkylammonium^{189,194} lead iodides with the reported γ_{LO} of 25-120 meV. A relatively strong coupling was observed in phenylethylammonium lead bromide with the strength of over 270 meV¹⁹⁵. Electron (exciton) – phonon interactions can be expressed by deformation potential D_{cv} , related to electron-phonon interaction strength through the equation

$$\gamma_{LO} \cong \frac{\hbar M \omega}{\rho L} \left(\frac{D_{cv}}{\hbar \omega} \right)^2, \quad (5.15)$$

where M is the sum of electron and hole effective masses, ρ is density, L is the thickness of the quantum well⁷³. Deformation potential in buthylammonium and phenylethylammonium lead halides ($6-15 \times 10^8$ eV/cm)^{73,125} is slightly exceeding that in MoS₂ (4×10^8 eV/cm)⁷³. Here the anisotropic deformation potentials of (ImEA)[PbI₄] along b and c direction are 9.6×10^8 eV/cm and 2.1×10^9 eV/cm, respectively.

Strong electron-phonon coupling is typical for corrugated and highly distorted layered perovskites. In many cases, the interaction is strong enough to cause self-trapping of excitons^{41,128,196,197}. The increase of interaction strength is associated with the highly polar metal-halide framework of the distorted octahedra causing significant deformation potential, which is a good trap for the tightly bonded within 2D layers excitons¹⁹⁶.

Surprisingly, the best fit was achieved with optical phonon energies of 35 meV (282 cm⁻¹) and 29 meV (234 cm⁻¹), that is significantly higher than the energy of the phonons corresponding to the inorganic sublattice, which are also higher than reported in the other 3D and 2D (11-22 meV)^{123,125,181,189,198} perovskites. The contribution to exciton-phonon coupling of higher energy (organic) phonons with energies of 39-46 meV has been previously demonstrated in case of phenylethylammonium lead iodide¹²⁶. The phenomenon was directly observed from absorption and photoluminescence spectroscopy at 15 K as phonon replicas. However, Thouin et al. disproved that

explanation and the fine structures of exciton emission was accounted for the polaronic nature of exciton-phonon interactions^{181,199}. Later, coupling with higher energy phonon was shown again in phenylethylammonium lead bromide ($E_{LO} = 50$ meV)¹⁹⁵, and alkylammonium lead iodides ($E_{LO} = 26$ -39 meV)¹⁹⁴.

For better understanding of the nature of the involved phonons in (ImEA)[PbI₄] perovskite, we performed DFT calculations of the vibrational modes in Γ point (Figure 5.7a) and compared them with the experimental Raman spectra (Figures 5.7b, c). The modes below 20 meV or 160-170 cm⁻¹ were found to be contributed by vibrations of the inorganic framework coupled with the molecules, above these frequencies – by the organic molecules, in good agreement with previous works^{15,44}. In order to simplify assignment, temperature dependent analysis was performed. The vibrations of interest are in the range between 24 and 35 meV, 190 and 285 cm⁻¹; three Raman bands were observed in the range. The peaks around 200 and 250 cm⁻¹ continuously sharpen with temperature decrease that can be caused by strengthening of hydrogen bonding⁴⁴,

Figure 5.7. Comparison of the calculated vibrational modes (a) and the experimental Raman spectra, measured at various temperatures (b, c) in the range below 400 cm⁻¹. Section *b* corresponds to vibration contributed by inorganic and cooperative organic-inorganic sublattices, vibrations at section *c* correspond to the vibrations of the organic molecules, and intensity of this part was increased for clarity.

so they are likely to correspond to torsion rotation of NH_3 . That is in good agreement with the results of DFT. The peak at 280 cm^{-1} , less sensitive to the change of temperature, was assigned to the vibration contributed by distortion of the imidazolium ring and NH_3 bending. The modes at 250 and 280 cm^{-1} or 31 and 35 meV fit the frequencies obtained from exciton-phonon coupling best. Despite the good fit, these modes are not LO phonons and they exhibit similar angular dependence (Figure 5.2 g, h), so they are hardly responsible for the anisotropic exciton-phonon coupling. Exciton-phonon coupling in $(\text{ImEA})[\text{PbI}_4]$ is likely contributed by both LO phonons from inorganic and organic subtleties with contribution from the organic part being more significant under excitation along b direction, which corresponds to the “zigzag” direction.

Thus, $(\text{ImEA})[\text{PbI}_4]$ exhibits strong and direction-dependent exciton-phonon interactions. Thereby, the anisotropic coupling between excitons and LO phonons causes broadening of photoluminescence peak, with different extent under excitation along b and c axes. Since the interactions are stronger along b axis, the corresponding photoluminescence peak is more red-shifted. That contributes to the angle dependence of the energy of PL photoluminescence peak maximum at higher temperatures.

However, in addition to the discussed peak broadening, the photoluminescence anisotropy might be contributed by polaron-related fine structure of the spectra, demonstrated previously in phenylethylammonium lead iodide^{181,199}. The results we discuss here mainly involve the dependence of photoluminescence on the polarization of the excitation only, while the polarisation of detection matters too. Preliminary results of photoluminescence study in parallel- and cross-geometry of excitation and detection polarisation are shown in supplementary information (Figure 5.8). While excitation along c axis always yields higher energy emission, the photoluminescence detected specifically along c axis is of lower energy. Besides, the remaining question is why the polarisation of the excitation source causes the anisotropy on emission, particularly considering the non-resonant, above-band gap energy of the laser. Therefore, the detailed mechanism of the unique anisotropy of photoluminescence is still to be studied and will be published elsewhere. For more detailed study of the phenomena, time resolved methods are needed along with photoluminescence study at cryogenic temperatures.

Figure 5.8. PL peak energy dependent on the geometry of the experiment. Polarisation of the excitation light was set as linear along b , c , between them ($\sim 45^\circ$), and circularly polarised (left and right). The signal was detected without polariser, and with the one oriented along c or b axis.

5.2.3. Anisotropic photoconductivity

A single crystal with previously identified crystallographic directions was chosen to investigate the electrical anisotropy. Pt electrodes were sputtered onto the crystal surface through a shadow mask (Figure 5.9a). First, we performed the measurements of DC photo-conductance along b and c directions of the crystal in the dark and under non-polarised illumination (100 mW/cm^2). I-V dependence is linear (Figure 5.9b), confirming a good Ohmic contact. Photocurrent exceeded the dark one by $2\text{-}2.7 \times 10^3$ times – the same order of magnitude as in the previously reported 2D perovskite, and significantly more than in some other semiconductors²⁰⁰. Such a big difference of photo and dark conductivity is likely to be due to low intrinsic concentration of free carriers in the sample²⁰⁰.

The photo conductance was found to be anisotropic, under non-polarized illumination, the ratio of photo conductance along c and b directions is 1.4 (Figure 5.9c). Thus, c axis corresponds to higher mobility, that is in good agreement with the other anisotropic 2D materials in “armchair” direction^{166,167}. Electrical anisotropy is usually explained by the difference of the effective electron and hole masses along a ,

b and c directions^{178,201}. The effective masses in in-plane directions along b and c axes, shown in table 2, were calculated by first principles method. Both hole and electron effective masses are significantly lower along c axis, indicating higher carriers' mobility along the perovskite layer “wrinkles” than across them and thus, better conductivity.

Table 5.3. Values of the effective electron and phonon masses obtained from first principle calculations.

	Along c axis		Along b axis	
	Γ -Z	X-H	Γ -Y	X-A
Electron effective mass	0.12	0.12	1.82	1.56
Hole effective mass	0.33		2.21	

The second experiment was to demonstrate the polarised photocurrent response. Photocurrent was measured along b and c directions of the crystals with adjustable orientation of the incident light polarisation. Dependence of photo conductance along b and c axes on the angle between the current direction and orientation of the light polarisation is shown in Figure 5.9d. It exhibits periodic dependence with conductance reaching the maximum when the light polarisation is perpendicular to the direction of the electrical measurement in both the cases. Similar dependence was observed in (BA)₂(MA)[Pb₂I₇], with rotating polarisation between in-plane and out-of- plane directions of the perovskite²⁰⁰. The conductance variation is more prominent when current is along b direction. This phenomenon of the in-plane photo conductance's anisotropy can be utilized for polarized light detection.

Figure 5.9. a) Optical microphotograph of the crystal with deposited Pt electrodes; b) I-V curve in the dark and under non-polarised illumination; c) photo (orange dots) and dark (black dots) conductance along b and c directions; d) conductance along b and c axes vs angle between the axis and illumination polarization.

5.3. Conclusions

In summary, we report the first observation of in-plane anisotropy in 2D hybrid perovskite, (ImEA)[PbI₄], imidasolium ethyl ammonium lead iodide formed by 3×3 <110> oriented perovskite folds. The material combines the advantages of 2D perovskites and anisotropic layered materials, exhibiting 2D properties in bulk form and in-plane anisotropic response. Raman spectroscopy is utilized for determination of the crystal orientation, since Raman modes are highly dependent on the relative direction of the crystal and the excitation laser polarization. Optical anisotropy is demonstrated experimentally by photoluminescence and reflectance spectroscopy and theoretically by first principles calculations. In contrast to the typical

photoluminescence anisotropy where the intensity of the peak is periodic, we show periodic variation in the emission energy. This is the first time that in-plane anisotropy in photoluminescence peak energy has been observed, and we believe this is contributed by variation of the PL peak width due to anisotropic exciton-phonon coupling, the detailed mechanism is to be reported in the future. Polarisation-direction dependent optical and electronic properties make (ImEA)[PbI₄] perovskite an outstanding candidate for novel devices, for instance, polarised light detectors and tuneable light emitters.

5.4. Methods and Materials

Synthesis and crystallographic characterisation ImEAPbI₄ single crystals were grown by solution technique described in ref 165. Formation of the corrugated structure and coincidence of the crystal shape and in-plane orientation of the crystals was confirmed by single-crystal X-Ray diffraction on a Bruker SMART APEX 2 system. A simple matrix collection was ran followed by a face-indexing routine whereby faces of the crystal are assigned (*hkl*) values based on the known geometry of the crystal and the position of the recorded diffraction peaks. The program APEX2 by Bruker was used to do this.

Optical spectroscopies Raman, photoluminescence and reflectance spectroscopies were conducted on A WITec Alpha 300RAS confocal Raman microscope (20× Nikon objective NA0.35, WD24mm, spot size of ~2 μm). The above band gap 633 nm linearly polarized He–Ne gas laser line was used for recording Raman spectra. Laser power was kept as 10 mW and integration time of 10 s to obtain sufficient Raman signal. The measurement was carried out in backscattered geometry. The signal was coupled to the non-polarization conserving fibre to ensure that detection was not affected by polarization. Passing through two 633 nm BragGrate Notch Filters (BNF), the signal reached Acton spectrometer (grating of 1800 grooves/mm) and a thermoelectrically cooled Andor CCD detector.

Linearly polarized DPSS 457nm laser with excitation power, maintained below 10 μW (5 s integration time) to avoid laser heating and degradation, was used to excite photoluminescence. A halogen lamp (15 V, 150 W, 3100 K) served as the white light

source for the reflectance measurements (50 s integration time). Low temperature spectra were collected between 293 K and 78 K using a nitrogen gas flow Linkam Stage. Linear polarizers and $\lambda/2$ wave plate were used to control the polarization of the incident and detected light. Scheme of the angle resolved experiments is shown in Figure 5.10. For linearly unpolished excitation we used $\lambda/4$ wave plate was applied, so the sample was excited by circularly polarized light instead. A linear polarizer was placed on the detection pass when needed to control the polarization of the signal.

Figure 5.10. Scheme of the polarization resolved optical experiments.

Fitting the reflectivity spectra The experimental reflectance spectra, collected at 80 K, were fitted by KK-constrained variational dielectric functions with use of RefFIT software⁵³, as described in Chapter 2.1.2 in details.

First principles calculations The atomic structure optimization, band structure and electron density simulations were performed on the basis on the density functional theory (DFT) with the code of Vienna *Ab initio* Simulation Package (VASP)²⁰². Atomic crystal structure, obtained by single crystal X-Ray diffraction at 100 K was used as the initial parameters. The exchange correlation potential was described using the functional of Perdew, Burke and Ernzerhof (PBE) within the frame of generalized gradient approximation (GGA)²⁰³. For the relaxation of structure, the Brillouin zone was sampled by $2 \times 1 \times 2$ k-point mesh using Monkhorst-Pack (MP) method and the energy convergence was chosen to be less than 10^{-5} eV/Å. Generally, many-body calculations beyond DFT need to start from the wave functions of the ground states and

thus it is critical to construct proper Kohn-Sham results for further quasiparticle calculations. In this work, we first carried out the ground states of ImEAPbI₄ using *ab initio* calculations as implemented in the QUANTUM ESPRESSO code²⁰⁴. The plane wave basis and norm-conserving pseudopotentials²⁰⁵ for the ion-electron interaction were adopted. We set a plane-wave cutoff energy of 50 Ry and a 2×1×2 Monkhorst-Pack k-point mesh. Then both GW and BSE calculations were carried out by using the YAMBO code²⁰⁶. For the optical absorption spectra, fifteen valence bands and fifteen conduction bands are included. We also considered the effect of spin-orbital coupling (SOC) during the calculations.

Photocurrent To measure the photoelectric transport properties of the crystals, patterned Pt electrodes were sputtered onto the crystal surface through a shadow mask. The photoconductivities of the single crystals were characterized by a pA source meter (4140B, Hewlett Packard) under white light illumination (halogen lamp see Figure for detailed spectrum). The irradiation intensity was kept at about 100 mW/cm², which was calibrated using a standard reference cell (91150V, Newport). Linearly polarized light was achieved by using a commercial Glan-Thompson polarizer (10GT04AR.14, Newport).

Chapter 6

Effect of the Thick and Soft Organic Sublattice on High Pressure Response in (HDA)₂[PbI₄] 2D Perovskite

6.1. Introduction

While chapter 5 is devoted to the unusual in-plane opto-electronic anisotropy in the 2D perovskite with the corrugated inorganic layers, the in-plane and out-of-plane directions are naturally different in all 2D perovskites. Particularly, it is reflected in their mechanical properties due to the hardness difference between the organic and inorganic layers.

In case of the hybrid 3D perovskites, the hardness and elastic modulus directly correlate with the Pb-X ($X = \text{Cl, Br, I}$) bond strength and the organic cations have no direct effect^{207,208}; their Young's modulus is in the range 10-30 GPa, and hence they are more compliant than the oxide ones. In case of the two-dimensional materials, the mechanical properties are anisotropic, differing between the in-plane and out-of-plane directions. The in-plane properties are similar to that of the 3D counterparts and are related to the covalent bond strength, while the out-of-plane features are related to the weaker Van der Waals intermolecular forces, leading to significantly decreased out-of-plane hardness. Qing Tu et. al. reported effect of the inorganic layer thickness and the organic spacer length on the hardness and the Young's modulus of the 2D perovskites^{209,210}. The Young's modulus of the 2D perovskites was demonstrated to be 3-7 times smaller than that of the 3D analogous, with the increase of the organic cation length leading to the further softening of the material. It is important to mention the tendency of the 2D perovskites to plastic deformations, that also affect their optical and electronic properties²¹⁰.

The compressibility and evolution of the structure under compression is related to the out-of-plane mechanical properties. Y. Qin et al. have reported a systematic study of the high pressure response in alkylammonium 2D perovskites with various lengths of the organic cation²¹¹. They demonstrated that materials with a longer alkyl chain are more compressible: the interlayer distance decreases more significantly with pressure, that is in good agreement with the smaller Young's modulus⁷. Introducing π - π interactions between phenyl rings in the organic molecules further decreases the interlayer distance changes⁷ in a good agreement with out-of-plane hardening⁷. Besides,

the softening of the inorganic layer causes a more complex evolution under compression. So $(\text{PEA})_2[\text{PbI}_4]$ (PEA = phenylethylammonium) with π - π interactions does not undergo any phase transitions^{212,213} in the low pressure range, while the alkylammonium compounds do, with the longer chain corresponding to more changes and more coexisting phases²¹¹.

In this chapter, we study the high-pressure response of the 2D alkylammonium lead iodide perovskite with a very long organic chain - hexadecyl ammonium (HDA) $\text{CH}_3(\text{CH}_2)_{15}\text{NH}_3^+$ - containing 16 carbon atoms: $(\text{HDA})_2[\text{PbI}_4]$; the crystal structure is illustrated in figure 6.1. This material exhibits high hydrophobicity and stability, and has been proposed for use in organic catalysis²¹⁴. Here we used optical techniques, photoluminescence, transmission and Raman spectroscopies, to investigate the evolution of the crystal and its band structure under compression in the range 0-20 GPa. PL mapping demonstrated that the crystals contained several domains with absorption and photoluminescence from the different electronic bands prevailing. Thus, on the boundaries of the domains p-n junctions are naturally formed. Notably, some domains were reversible after decompression, while some were not.

Figure 6.1. Crystal structure of $(\text{HDA})_2\text{PbI}_4$.

6.2. Results and discussion

6.2.1. Properties at ambient conditions

The photoluminescence (PL) and optical absorbance (OA) spectra of $(\text{HDA})_2[\text{PbI}_4]$, collected under ambient conditions, are presented in Figure 6.2a. The optical absorbance spectrum contains a prominent excitonic feature even at room temperature, typical for the 2D perovskites⁵⁶. The material exhibits intensive excitonic photoluminescence with a sharp, slightly asymmetrical peak, also typical for the 2D perovskites^{76,109,189}.

Figure 6.2. a) PL and optical absorbance spectra of $(\text{HDA})_2[\text{PbI}_4]$, collected under ambient conditions. b) Illustration of the in-plane $[\text{PbI}_6]$ octahedra tilting and Pb-I-Pb bond angles.

The OA and PL peaks are centered at 488 and 500 nm respectively, that is notably at higher energy than in the conventional 2D lead-iodides perovskites, such as $(\text{PEA})_2[\text{PbI}_4]$ (PL at ~ 527 nm)¹²⁴ and $(\text{BA})_2[\text{PbI}_4]$ (PL at ~ 525 nm)²¹⁵. Similar shorter wavelength PL (498 nm) has been reported in other 2D iodoplumbates with a long organic chains (dodecyl ammonium- and octadecyl ammonium lead iodides), and chloroanilinium tetraiodoplumbate (PL at 485 nm, OA at 473 nm), cyclopropyl ammonium tetraiodoplumbate (PL 502 nm at, OA at 485 nm)²¹⁶. The top of the valence band in lead iodide perovskites is contributed by the antibonding Pb s and I p orbitals; enhancing the interactions between them increases the energy of the band. The bottom of the conduction band is mainly contributed by the nonbonding state of Pb p orbitals, which is less sensitive to the orbital overlap between Pb and I^{211,217,218}. Thus, the band gap correlates with the overlap of Pb and I orbitals and so with the Pb-I-Pb angle and Pb-I bond length: shorter length and flatter angle correspond to a narrower bandgap. A schematic illustration of the bond and angle changes effect is shown in Figure 6.3. The Pb-I bond length criterion becomes significant under high pressure, but the Pb-I-Pb

angle variation affects the band gap at ambient conditions as well. The average Pb-I-Pb angles is 145.5° in $(\text{HDA})_2[\text{PbI}_4]$ (PL at 488nm) and 155.5° in $(\text{PEA})_2[\text{PbI}_4]$ (PL at 527nm)²¹⁶, in good agreement with the criteria. The other reason for the blue shift is the increased quantum confinement due to the larger barrier thickness^{212,216}.

Figure 6.3. Illustration of the Pb-I-Pb angle and Pb-I bond length changes and its effect on the CVM (conduction band maximum) and VBM (valence band minimum).

In-situ high pressure Raman study was performed to identify the vibrational properties and the phase transitions. The ultra-low wave number (a) and high wave number (b) spectra under pressure are shown in Figure 6.4. The pressure range for the ultra-low wavenumber was limited to 2 GPa only as we needed to use the 633 nm laser for this wavenumber range due to the availability of the Bragg diffraction gratings. Above 2 GPa, the samples show strong PL emission which completely masks the Raman peaks. In the high wavenumber range, we used the 785 nm laser which can effectively avoid the strong PL emission from the sample and hence we could record Raman spectra at higher pressure. The peaks below $150\text{--}200\text{ cm}^{-1}$ are mainly contributed by the vibrations of the inorganic sublattice, with the bands below $\sim 70\text{ cm}^{-1}$ being assigned to the bending and tilting of the $[\text{PbI}_6]$ octahedra, and the rest corresponding to the symmetrical and asymmetrical stretching of Pb-I bonds^{15,156,165,179}. The peaks in the high wave number region (Figure 6.4b) are contributed by the molecular vibrations of the organic HAD cation. The ranges assigned to the characteristic vibrations of the HDA functional groups are highlighted in the Figure 6.4 b: the green area corresponds to C-N stretching ($\nu\text{ CN}$), the yellow one – C-C stretching

(ν CC), the blue one – wagging (w) and bending (δ) of the CH_2 and CH_3 groups, and the pink one – stretching (ν CH and ν NH) of C-H and N-H bonds²¹⁹.

Figure 6.4 The ultra-low wave number, 633 nm excitation (a) and high wave number, 785 nm excitation (b) in-situ Raman spectra of $(\text{HDA})_2[\text{PbI}_4]$ under increasing pressure. a) The range in the red frame ($75\text{--}200\text{cm}^{-1}$) is zoomed in for clarity. The gray dash arrows show the evolution of the peaks, the solid pink arrows indicate the phase transition. The peaks, highlighted in (b), correspond to the HDA molecules, the other peaks are contributed by the DAC and pressure medium. c) In-situ pressure dependent b) optical absorbance spectra in the low-pressure range.

Under compression from 0 to 0.77 GPa and from 0.85 to 2 GPa, the bands assigned to the inorganic lattice vibrations and most of the molecular bands undergo a continuous blue shift. The increase in the frequency is caused by the expected bond shrinkage with the pressure increase³⁵. The shape of the spectrum undergoes significant changes from 0.77 GPa to 0.85 GPa, attributed to a phase transition. The two peaks at ~ 80 and $\sim 100\text{ cm}^{-1}$ turn into one. As these peaks were assigned to the Pb-I bands stretching, this may indicate that the phase transition decreases the octahedral distortion and tilting as the Pb-I bonds become more similar. The peaks below 75 cm^{-1} , contributed by octahedra tilting and bending, undergo a red shift during the transition. Most of the changes happen between 0.77 and 0.82 GPa, but a new peak at 32 cm^{-1} appears between 0.82 and 0.85 GPa, that may be an indication of a phase transition as well. However, one progressive transition taking place in a pressure range is more likely, as such gradual changes are typical for the effect of high pressure²¹¹. The organic sublattice is also involved at the phase transition, as confirmed by the high wave number Raman spectroscopy (fig 6.4 b). The shape of the spectrum changed between 0 and 0.9 GPa, particularly the ν CN and δ CH_2 , CH_3 peaks.

The further compression to 2 GPa did not demonstrated changes in the inorganic vibrations except the continuous blue shift of the major bands. Reaching 2.8

GPa yielded photoluminescence (with 633 nm excitation) and so disappearance of the Raman signal that, in good agreement with the absorption spectrum, demonstrated onset of absorption at this pressure. Above 1.5 GPa the new component in the absorption spectrum was found (Figure 6.4c) along with some minor changes in the Raman spectrum of the organic sublattice: splitting of the peak at 1070 cm^{-1} , corresponding to $\nu(\text{CC})$ and $\rho(\text{CH}_3)$, and changes in the broad band at 1460 cm^{-1} . Importantly, these changes correlate with the variations in the optical properties, which is discussed in detail below.

6.2.3. Optical Properties under Pressure

High pressure evolution of the optical properties is shown in Figure 6.5. The optical micrographs (Figure 6.5a) demonstrate the change of the color from yellow at 0 GPa to black at 7.4 GPa, with the color being notably non-uniform at 3-4 GPa. Thus, $(\text{HDA})_2[\text{PbI}_4]$ exhibits visually reversible piezochromism. Surprisingly, the absorption edge undergoes a red shift from 505 to 503 nm when the pressure increases from 0 to 0.69 GPa (Figure 6.4c), indicating that within this low-pressure phase tilting of the octahedra contributes to the tuning electronic structure more than the bond shrinkage. During the first phase transition at ~ 0.7 GPa, discussed above, the absorption edge and PL peak red shift by 50(5) nm. Such a significant red shift can not be caused by the bond length contraction alone and unambiguously demonstrates the Pb-I-Pb angle increasing. This conclusion is in good agreement with the Raman data.

Figure 6.5. Optical properties of $(\text{HDA})_2[\text{PbI}_4]$ in the pressure range up to 21.5 GPa. a) Optical images at selected pressures, the red line indicates the compression, the green one – decompression. In-situ pressure dependent b) optical absorbance spectra and c) normalized photoluminescence spectra.

Further compression causes the expected continuous red shift of the optical features, followed by appearance of the additional low energy component above 1.5 GPa and splitting to even more components above 10 GPa. A similar phenomenon was observed in $(\text{C}_8\text{H}_{17}\text{NH}_3)_2[\text{PbI}_4]$ and $(\text{C}_{12}\text{H}_{25}\text{NH}_3)_2[\text{PbI}_4]$ – another 2D perovskites with shorter (but still relatively long) acyclic chains²¹¹. The PL intensity variations are not significant, and the total PL peaks area reaches its maximum at ~ 4 GPa but starts to decrease above 6 GPa and is quenched at ~ 21.5 GPa. Upon decompression, both the PL and OA spectra differ from the original, in contrast with $(\text{C}_8\text{H}_{17}\text{NH}_3)_2[\text{PbI}_4]$ and $(\text{C}_{12}\text{H}_{25}\text{NH}_3)_2[\text{PbI}_4]$ whose optical properties are reversible with exception of 1-2 nm blue shift due to the size reduction²¹¹.

Y. Qin et al. proposed two models to explain the additional PL components in $(\text{C}_{12}\text{H}_{25}\text{NH}_3)_2[\text{PbI}_4]$ depending on pressure²¹¹. In the low-pressure range multiple peaks were assigned to the coexistence of the mixed phases confirmed by XRD. In the mid-pressure range the band gap narrowing was proposed to activate the trapped excitonic states; and the broad band emission at high pressure was accounted for the extrinsic self-trapped states.

Figure 6.6. Excitation intensity-dependent PL spectra a) in situ under 8.3 GPa compression; b) after decompression. Plot of the PL intensity vs excitation intensity (logarithmic scale) and linear fit to extract the power law coefficient k : c) under 8.3 GPa (total area of the PL) d) after decompression (the blue diamonds represent the area of the peak at 499 nm, the red pentagons – of the peak at 525 nm, black circles – the total area).

In (HDA)₂[PbI₄], the new phase above 0.85 GPa is unlikely to be mixed since both the PL and OA spectra below 1.5 GPa consist of one sharp component (Figure 6.5 b, c). Besides, Raman spectroscopy did not demonstrate a phase transition at 1.5 GPa (Figure 6.4a, b), when the optical spectroscopy clearly revealed the additional component. To test the trapped states theory, we performed excitation intensity-dependent PL study demonstrated in Figure 6.6.

The PL intensity grows in a power law function $I_{PL} = I_{laser}^k$, where $1 < k < 2$ is the power law coefficient that is dependent on the excitation intensity and recombination mechanism¹⁹⁷. For the given laser fluence ($>1 \text{ W/cm}^2$), $k = 1$ for free excitons^{132,220}. The other radiative and non-radiative mechanisms compete with the free exciton recombination; and depending on the probability of such processes, the k value is expected to grow²²⁰. Excitation intensity-dependent PL spectra, presented in Figure 6.6a, b, demonstrate that both under and after compression the main and additional components have similar power-dependent behavior. Linear fit of the PL intensities (of the components and total) vs excitation intensity yielded the k value close to 1, as shown in Figure 6.6c, d. The $k = 1$ is not typical for extrinsic trapped states^{133,221}. Thus, the origin of the additional components is unlikely to be the defect states.

The effect of anisotropy of the mechanical properties in 2D perovskites on high pressure response has been recently discussed in several publications. Gang Liu et al. reported two regimes under pressure in (BA)₂(MA)[Pb₂I₇]: layer-to-layer compression mainly dominated the soft organic part followed by changes in the inorganic part at higher pressure²¹⁸. Y. Qin et al. also suggested disordering of the soft organic sublattice occurring at lower pressure than the total amorphisation²¹¹. Chaofeng Gao et al. proposed the organic layer to play a role of a spring, being compressed faster than the lead iodide octahedra and working as a protection of the inorganic layer against the octahedra distortion and rotation^{213,222}.

6.2.4. In-situ PL Mapping

Notably, in (HDA)₂[PbI₄], the organic layer is thicker and softer, and the anisotropy of the mechanical properties is much stronger^{209,210}. Moreover, the long

alkyl

Figure 6.7. In-situ high pressure PL mapping, 457 nm excitation. a) Optical micrographs at various pressures; b) PL intensity mapping (the color scheme corresponds to the total PL area); c) position of PL maximum mapping at the corresponding pressure.

Figure 6.8. a) The domains with different optical properties marked on the PL position map collected at 3.2 GPa, and b-f) the corresponding to the 6 domains PL spectra, measured in-situ at 0, 3.2, 5.2, 8.3, decompressed, respectively.

chain containing sixteen carbon atoms has more degrees of freedom to respond to the compression in comparison with relatively short and rigid phenylethylammonium cations. Interestingly, we noted that the optical properties under pressure are non-uniform in (HDA)₂[PbI₄], which was not reported in other 2D perovskite materials. To investigate this phenomenon, we performed high pressure in-situ PL mapping of a crystalline sample, presented in Figure 6.7.

High pressure evolutions of the PL mappings based on the total photoluminescence intensity (area) is shown in row b, and that based on the spectral position of the main PL peak in row c (Figure 6.7). Before compression (0 GPa) the entire crystal exhibits relatively uniform photoluminescence: the variation of the peak position is within 1-2 nm (Figure 6.7c), that is close to the instrumental resolution; and the relative intensity is in the range of 60-100% (Figure 6.7b) which may be attributed to the variation in thickness and/or unevenness of the sample surface.

Under compression, at 3.2 GPa, the situation changes. The crystal is clearly separated into several domains with different PL energy and intensity. The domains are noticeable even from optical images: at 0 GPa the color of the crystal is relatively uniform (suggesting a relatively uniform thickness), while at 3.2 GPa some parts are darker than the other. The PL spectra, corresponding to the six distinctive areas of the crystal (Figure 6.8a – the map at 3.2 GPa) were chosen and plotted together in Figure 6.8b-f. At 3.2 GPa PL in the areas 1 and 5 is dominated by the component with the highest energy (blue in the corresponding mapping at 3.2 GPa). The domains 2 and 4 are dominated by the component at ~ 560 nm (orange areas), and the domain 3 – by the lowest energy luminescence (red area). PL intensity from the area 6 is the most blue shifted and vanishingly weak. Comparing Figures 6.7b and 6.7c at 3.2 GPa demonstrates that the domains with the lowest energy correspond to the highest emission intensity. These results are consistent upon further compression to 5.2 and 8.3 GPa, with the difference in both PL intensity and energy increasing.

After decompression, the right part of the crystal (blue area in Figure 6.7c at decompressed 0 GPa – domains 1, 3, 4, 6) appeared to be reversible: the PL spectra coincided with the ones before compression. The PL in the left part of the crystal (domains 5 and 0 – the orange area in Figure 6.7c at decompressed 0 GPa) was not

Figure 6.9. Different 2D perovskite samples after decompression: a-c) 3 samples from independent experiments - $(\text{HDA})_2[\text{PbI}_4]$; d-f) $(\text{PEA})_2[\text{PbI}_4]$. a, d) – optical images, b, e) PL position mapping, c, f) PL intensity mapping.

reversible with the second peak at 520 nm conserved. The left part of the crystal corresponds to the area containing many smaller domains under high pressure, in comparison with the right part. These results were proven reproducible – a similar phenomenon was observed in 3 other experiments including crystalline and powder $(\text{HDA})_2[\text{PbI}_4]$ samples (Figure 6.9a-c). Moreover, the change is persistent after 4 days and after heating at 60 °C for an hour. This phenomenon seems to be specific for 2D perovskites with a long organic chain, e.g. $(\text{PEA})_2[\text{PbI}_4]$ did not show the domain-like structure under pressure nor after decompression. In Figure 6.10 we propose a scheme of the high-pressure behavior of $(\text{PEA})_2[\text{PbI}_4]$ and the origin of the domains.

Before compression, according to the structural data, the HDA cations are linear and arranged perpendicularly to the inorganic layers (Figure 6.10a). Applied pressure significantly affects the organic cations, causing its bending (similar to the DFT calculated structures in ref. ²¹¹). Being long and soft (as a result of the long chains and the weak interactions between chains), the HDA cation possesses more degrees of freedom to respond the compression, i.e. the bending can take place in different carbon atoms, as highlighted by the red circles in fig 6.10b schematically, causing disordering of the organic sublattice. These different changes happen randomly in the volume of the crystal (or dependent on unknown factors). The different kinds of HDA bending and the different degree of disorder affect the band structure (Figure 6.10d-f) as they cause the changes in the inorganic layer through inorganic octahedra modifications and possibly the formation of defect states. The latter is unlikely to play an important role, because the lower energy states can also be detected from the absorption spectra and

Figure 6.10. a-c) Illustration of $(\text{HDA})_2[\text{PbI}_4]$ during compression - decompression process. The blue bars correspond to the inorganic layers, the zigzag lines with a green ball represent HDA cations. The red circles indicate the bending of the cations. d-f) The top of the valence band and the bottom of conduction band.

the excitation intensity dependent investigation did not reveal the traps-associated emission. As the $(\text{HDA})_2[\text{PbI}_4]$ crystals have a platelet shape, the domains with the different kinds of HDA bending can be observed by means of PL spectroscopy. After decompression, in contrast with the samples containing shorter organic molecules, the disordering is not completely reversible (Figure 6.10c), especially in the parts of the crystal with the maximum disorder under compression, and the residual disorder causes the additional PL component after compression.

6.3. Conclusions

Summing up, we have investigated the high-pressure evolution of $(\text{HDA})_2[\text{PbI}_4]$ 2D perovskite with a long organic cation, containing sixteen linearly arranged carbon atoms. A phase transition at ~ 0.7 GPa was demonstrated by means of Raman and optical spectroscopy. Furthermore, we proposed that variations and disordering of the organic cations leads to coexistence of the emission states, due to the formation of domains with different phases. Notably, this process was shown to be partly irreversible, in contrast with the other alkylammonium lead iodide perovskites. To further support

our proposed crystal and electronic structure evolution, some additional investigations, such as DFT simulations and high pressure XRD study, are desirable. The work demonstrates how optical properties of one material can be modified in different ways, creating technologically important phenomena, such as enhanced PL emission, structural stability, or formation of local p-n junctions at the domain boundaries.

6.4. Methods and Materials

Synthesis 1-Hexadecylamine (HDA, 98%) precursor, purchased from Merck, was used without additional purification. PbI_2 (99.999%) was purchased from Sigma-Aldrich. HI (57% wt. aq.) was purchased from TCI. Tetrahydrofuran (THF) was distilled and stored in a glove box upon use.

Hexadecylammonium hydroiodide (HDAI): HDA (1.8 g, 7.5 mmol), 1.1 mL of HI (57% wt. aq.) and 20 mL methanol were being stirred for 3 h at 0 °C. Then a rotary evaporator was used to remove the solvent. The residue was further dissolved in ethanol to give a concentrated solution; a white solid was obtained upon diethyl ether added. Then the precipitate was washed with diethyl ether three times. The product was stored in a glovebox (2.55 g, 92% yield). ^1H NMR ($\text{DMSO}-d_6$, 500 MHz): δ = 0.85 (t, J = 6.8 Hz, 3 H), 1.24 (bs, 26 H), 1.50 (q, J = 7.5 Hz, 2 H), 2.71 – 2.81 (m, 2 H), 7.58 (s, 3 H) ppm. MS (ESI^+ , m/z) calculated for $\text{C}_{16}\text{H}_{36}\text{N}^+$ [M^+] m/z 242.46, found 242.23. Elemental analysis results (%): C, 52.23; H, 9.64; N, 3.96 (calculated (%): C, 52.03; H, 9.82; N, 3.79).

Hexadecylammonium lead iodide $(\text{HDA})_2[\text{PbI}_4]$ perovskite: Stoichiometric amounts of the HDAI salt (184 mg, 0.500 mmol) and PbI_2 (115 mg, 0.250 mmol) were added to 5.0 mL of THF and stirred for 2 h at room temperature. Vapor diffusion of diethyl ether into the obtained clear yellow solution yielded yellow flakes of the perovskites (136 mg, 52% yield). Elemental analysis results (%): C, 32.22; H, 5.83; N, 2.43 (calculated (%): C, 32.03; H, 6.06; N, 2.34).

High pressure generation. The diamond anvil cells (DAC) with a culet diameter of 400 and 500 μm was used to generate high pressure up to 20 GPa. The crystalline or powder samples a hole of ~ 200 μm diameter in a preindented stainless-steel gasket with a thickness of ~ 40 μm . In case of single crystal samples, the silicone

oil was added as the pressure-transmitting medium to create hydrostatic pressure. In case of the powder sample, no pressure medium was used, and the powder was compressed directly. Ruby powder was placed into the DAC as a reference to determine the pressure value. Refer to Chapter 2.1.2 for more detailed description of the high-pressure experiments.

Sample preparation Single crystals of $(\text{HDA})_2[\text{PbI}_4]$ were chosen for most of the experiments with the following exceptions: exfoliated with Scotch tape flakes were used for transmission measurements at ambient conditions; the grinded powder sample was used in one of the high-pressure experiments, including the high wave number Raman with 785 nm excitation and PL mapping.

In-situ photoluminescence and transmittance measurements. The WITec alpha 300RAS confocal Raman microscope was used to record photoluminescence and transmittance spectra. To obtain the photoluminescence, the blue line of a linearly polarized CW solid laser (457 nm) line was chosen. The low excitation power was kept (1.3 μW) to avoid photo degradation and saturation of the detector except for the power dependent experiment. In case of in-situ the single spectrum PL measurements, the integration time was 10s, in case of the PL mappings – 0.035s. A halogen lamp (15 V, 150 W, 3100 K) was used as the white light source for the absorption measurements (integration time 10 s). Spectra were collected with an Acton spectrometer with a diffraction grating of 150 grooves/mm and a thermo-electrically cooled Andor CCD detector. Long working distance 20 $\times$ (Nikon NA0.35, WD24mm, spot size of $\sim 2 \mu\text{m}$) and 50 $\times$ (Olympus, FN26.5, NA0.35, WD20mm, spot size of $\sim 1 \mu\text{m}$) microscope objectives were used for all the experiments. Optical absorption spectra were calculated by the formula $OA = \log(-I_{Tr}/I_{WL})$, where I_{Tr} is the transmission signal from the sample, I_{WL} is intensity of the white light.

In-situ Raman measurements. The WITec alpha 300RAS confocal Raman microscope was used to collect to low wave-number Raman spectra with 633 nm (red) line excitation from the a He–Ne gas laser with a power of 7-10 mW and integration time 100s. Spectra were collected with an Acton spectrometer with a diffraction grating of 1800 grooves/mm (1.3 cm^{-1} resolution) and two 633 nm BraggGrate Notch Filters (BNF) for effective laser line rejection. detection is described in the previous

paragraph. Raman spectra with 785 nm excitation were collected by inVia confocal Raman microscope, with a diffraction grating of 1200 grooves/mm and 785nm notch filters, in the range from 100 cm^{-1} to 3300 cm^{-1} and integration time 30s. A long working distance 20 $\times$ (Nikon NA0.35, WD24mm, spot size of $\sim 2 \mu\text{m}$) microscope objective was used.

Chapter 7

Conclusions and Outlook

7.1. Summary and Conclusions

Hybrid organic-inorganic perovskites are among of the most studied materials in the last few years. Particularly, the low dimensional perovskites have been demonstrated to be excellent candidates for applications in various technologies, such as solar cells, LED, spintronics, lasers, magnetic and ferroelectric devices, and so on. A clear understanding of the fundamental properties is critical for new 2D-perovskite based technologies. A great progress has been achieved in this field recently, and we are pleased that this work has made its contribution to the development and understanding of these outstanding materials. In this thesis, we have systematically demonstrated how variations of the organic cation in 2D perovskites affect its structural and optical properties and bring up special, exclusive features.

1. Effect of mixing two types of organic cations – a long interlayer chain and a small one, able to fit into the cuboctahedral cavities one – has been investigated in case of $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ (phenylethylammonium - methylammonium lead iodide) perovskite. Correlating methyl ammonium cation vibrations and excitonic features revealed a phase transition happening in a wide range between ~ 150 and 200 K. Thus, we demonstrated the importance of methylammonium dynamics even in 2D perovskites with a smaller portion of MA ions.
2. Use of a relatively short asymmetric bication (imidazolium-ethylammonium) as an organic part resulted in a 2D perovskite with corrugated inorganic layers. For the first time, we demonstrated in-plane anisotropy in $(\text{ImEA})[\text{PbI}_4]$ perovskite: photoconductivity, vibrational modes, the optical constants, and exotic variations of the photoluminescence energy. The latter was accounted for by the anisotropic exciton-phonon coupling, which contributes to the shift of the photoluminescence peak maximum. The materials were shown to combine the unique properties of hybrid halide perovskites and in-plane anisotropic potential of two-dimensional materials.

3. Use of a very long organic cation has increased quantum and dielectric confinement along with the band gap. Effect of the long and soft organic cation on optical properties and structural stability has been demonstrated in $(\text{HAD})_2[\text{PbI}_4]$ 2D perovskite. By means of the in-situ optical techniques: photoluminescence, transmission and Raman spectroscopies, we investigated the evolution of the crystal and band structure under compression in the range 0-20 GPa. We demonstrated that under compression the crystals contained several domains with varying photoluminescence associated with transition between different electronic bands.

7.2. Future work

7.2.1. Effect of incorporated water and conformational isomerism in 2D perovskites

Chapter 4 of this thesis is devoted to studying the disorder of the organic molecules in 2D perovskites. The focus of the work was hydrogen bonding of the methylammonium cations, however we have also discovered some disorder in the bulk phenylethylammonium cation by solid state NMR study (Figure 4.2), that was accounted for coexistence of two conformational isomers of the PEA molecule – anti and gauche.

Figure 7.1. Raman spectra of PEA⁺ (salt of the organic cation) – black line, $(\text{PEA})_2[\text{PbI}_4]$ ($n = 1$) – orange line, fresh $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ ($n = 2$) – light red line, and $(\text{PEA})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ after exposure to humid air ($n = 2$ old) – dark red line.

This hypothesis was tested by Raman spectroscopy, that demonstrated ambiguous results. Figure 7.1 demonstrates Raman spectra of 4 samples: PEA₂I (salt of the organic cation), (PEA)₂[PbI₄] (*n* = 1), fresh (PEA)₂(MA)[Pb₂I₇] (*n* = 2), and (PEA)₂(MA)[Pb₂I₇] after exposure to humid air (*n* = 2 old).

The spectrum of PEA₂I clearly corresponds to anti-conformation, while that of the *n* = 1 sample and of the fresh *n* = 2 sample correspond to gauche-conformation²²³. The spectrum of the old *n* = 2 is of worse quality, that may be related to occurrence of the disordering, and the peaks might correspond to both gauche and anti-conformations. However, the noise does not allow to derive an unambiguous conclusion.

Figure 7.2: ¹H MAS NMR spectrum of PEA₂MAPb₂I₇ ($\nu_0 = 800.16$ MHz, $\nu_r = 35$ kHz) demonstrating a growing H₂O resonance (marked with an asterisk) commensurate with increasing times of atmospheric exposure.

We also noted increasing of water content after exposure to air of the sample used for NMR analysis, as demonstrated in Figure 7.2. This sample was in powder form, while the single crystals with less surface area and therefore less exposed to water were

used for Raman study. Thus, we suggest absorption of water is to drive the disordering in the PEA layers.

2D perovskites are believed to be relatively moisture stable^{102,197}, that is one of their main advantages in comparison with the 3D counterparts. Even adding small fractures of 2D perovskites significantly increased stability of 3D perovskite-based solar cells^{103,104}. Our preliminary results demonstrated that water may play an important role in disorder and molecular dynamics in 2D perovskites. Thus, this research is to be continued and applied to the other 2D perovskites.

7.2.2. Anisotropy in 2D perovskites

Optical and physical anisotropy in 2D materials, such as black phosphorous, has been extensively studied in recent years and can be utilized for various applications, including electronics, optoelectronics, thermoelectric, piezoelectric, and ferroelectric devices. In-plane anisotropy in 2D perovskites may bring about a significant technological benefit due to their simple preparation and low price. Thus, more anisotropic 2D perovskites are to be discovered, and oriented films fabrication techniques are to be optimized.

In this thesis, we report in-plane optical anisotropy in (ImEA)[PbI₄] perovskite. We have demonstrated the effect of strong anisotropic exciton-phonon coupling on the shift of the photoluminescence peak maximum. However, the detailed mechanism of the unique anisotropy of photoluminescence is to be studied further. We have studied the effect of the polarization of the excitation light but have not discussed the polarization of the emitted light, which may clarify the mechanism. Moreover, a spectroscopy study at liquid helium temperatures may be the next step.

7.2.3. Two-Dimensional Perovskites with Functional, Optically-Active Organic Cations

By now, one of the most promising direction is development of low-dimensional, including two-dimensional, perovskites with a functional organic part. Normally, the organic cation plays an important, as shown in this thesis, but indirect influence^{25,37,38}, playing a role of a barrier in a quantum wall (wire, dot) system.

However, in recent 1-2 years, more compounds with optically active organic cation have been investigated.

Sudeep Maheshwari *et. al.* published a computational work, predicting the possibility of interlayer charge transfer. As shown in Figure 7.3, the bottom of the conduction band is localized on the inorganic sheets, while the top of the valence band corresponds to the organic cation. The energy of the latter can be tuned by changing the electron withdrawing/donating character¹²⁰.

Figure 7.3. a) Illustration of charge transfer between organic and inorganic layers in 2D perovskites; b) Corresponding DFT calculated band structure: bands plotted in blue are localized on the inorganic layers and bands in red are localized on the organic cation. Reprinted from ref.¹²⁰.

Moreover, Nadège Marchal *et al.* reported a 1D perovskite where the organic part comprises of a donor–acceptor charge transfer complex between pyrene and tetracyanoquinodimethane, $(C_{20}H_{17}NH_3)[PbI_3] \cdot (C_{12}H_4N_4)$. In this compound the organic part is responsible for the optoelectronic properties and charge transfer, while the inorganic part plays a role of a structural skeleton²²⁴.

María C. Gélvez-Rueda reported charge separation in the 2D perovskite with a similar organic part – pyrene-tetracyanoquinodimethane donor-acceptor complex (Figure 7.4). The optical features of the perovskite were shown to be contributed by the organic charge-transfer complexes (fig 7.4.b)²²⁵.

Figure 7.4. Illustration of the structure (a) and absorption spectra (b) of 2D lead-iodide perovskite with pyrene-tetracyanoquinodimethane donor-acceptor complex as organic layer. The spectrum in red represents a perovskite with an inactive organic cation for comparison, green – a salt of the donor-acceptor complex, blue – the perovskite with the optically active organic cation²²⁴.

High-pressure studies of such materials are of particular interest. High pressure tends to strengthen the bonds and interactions between the components. Thus, increase of charge transfer, conductivity and other properties are expected to be observed under compression.

7.2.4. Fluorinated cations as the organic part in hybrid 2D perovskites

Halogenation, particularly fluorination of the organic cations, has been another way of functionalizing 2D perovskites. Multilayer 2D perovskites with fluorinated phenylethylammonium or ethylammonium organic spacers have repeatedly demonstrated significantly improved charge transfer, absorption and moisture and thermal stability in solar cell applications^{226–231}. The improvement was attributed to several factors: film quality and orientation of layers^{229,230}, shorter interlayer separation with better aligned stacking²³¹. Besides, the polarity of fluorine atoms is believed to drive the charge separation²²⁹.

However, most of the works on the fluorinated 2D perovskites are related to energy harvesting, while the fundamental reasons for these outstanding properties remain unclear. A systematic study of these materials is needed for better understanding of the fluorine effect, including a high-pressure study to test the fluorine influence on π - π interactions.

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