Probing carrier and phonon dynamics in halide perovskites using ultrafast terahertz spectroscopy

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Probing Carrier and Phonon Dynamics in Halide
Perovskites Using Ultrafast Terahertz
Spectroscopy

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Jan 2018

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the degree of Doctor of Philosophy

**Division of Physics and Applied Physics
School of Physical and Mathematical Sciences**

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Abstract

The development of photovoltaic devices based on semiconductors requires a clear understanding of charge-carrier and phonon dynamics on an ultrashort time scale after a photoexcitation. Transport processes are related to lattice vibration modes via carrier-phonon coupling, which determines the unique properties of the material.

As a promising next-generation solar cell material, lead halide perovskites show excellent photovoltaic performances, which triggered a flurry of intense research. Terahertz (THz) radiation can be absorbed by free charge carriers, therefore is suitable to probe the transport properties with a contact-free manner. Moreover, the low-lying optical phonon modes lie in THz range as well. Therefore, terahertz time-domain spectroscopy (THz-TDS), especially the time-resolved terahertz spectroscopy (TRTS), is an excellent tool for probing carrier and phonon dynamics in halide perovskites.

Temperature evolution of low-frequency phonons in MAPbBr₃ is performed over a range of 20–300 K. We observed phonon mode splitting at the orthorhombic–tetragonal phase transition temperature. Furthermore, both transverse-optical and longitudinal-optical (LO) phonon modes at 300 K are identified from the THz-TDS spectra. We further use these LO phonon mode frequencies to calculate carrier mobility using Feynman’s polaron theory.

TRTS study on FA_{0.85}Cs_{0.15}Pb(I_{0.97}Br_{0.03})₃ thin films shows that upon the photoexcitation, both photo-generated charge carriers and photo-induced change in optical phonon modes contribute to the photoconductivity. We observe a delicate interplay between carriers, phonons and excitons that govern the photo-physical

phenomena of the perovskites. Our data show that the combination of phonon emission during carrier relaxation, phonon-assisted exciton dissociation and photo-enhanced carrier screening, ensure a large and long-lived free-carrier population in the system, especially at room temperature.

Organic-ligand treated and pristine $\text{MAPbI}_{3-x}\text{Cl}_x$ thin films are comparatively studied by TRTS. The dynamics of photo-generated carriers in both thin films are investigated, and modeled by the Drude model. Both samples show high carrier mobility ($100\text{s cm}^2\text{V}^{-1}\text{s}^{-1}$) and long diffusion length (several microns).

Stability study on $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) thin films is performed by THz-TDS via monitoring the changes in THz phonon modes, by X-ray diffraction measurements to obtain the crystal structural information, by scanning electron microscopy to investigate the morphology changes under various conditions.

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Chapter 1

Introduction

In this chapter, the motivation of my thesis work will be introduced. The organization and contents of each chapter will be presented at the end of this chapter.

1.1 Motivation

The development of Light Amplification by Stimulated Emission of Radiation (LASER) since 1960s marked the beginning of a new era to explore the universe from detecting the gravitational waves to analyse chemicals. The laser differs from other light sources by their high spatial and temporal coherence with collimated propagation. Over the next few decades, laser pulses as short as a few-femtosecond (few-fs) were produced, resulting in great advancement in the field of ultrafast dynamics [1]. The driving force behind this interest is the potential of ultrafast devices made of novel materials and the endless need for faster response. To improve the performance of these devices and address these urgent needs, a fundamental understanding of various dynamical processes in various materials is necessary. Therefore, the photoexcitation of materials out of their equilibrium and probing the subsequent dynamics on an ultrashort time scale, have become a key research area.

Pump-probe techniques with proper data acquisition electronics allow researchers to probe extremely short-lived processes, whose time resolution is only limited by the

laser pulse duration [2,3]. Since the speed of light in vacuum is independent of the light wavelength (photon energy), the time delay between two pulses split from the same laser source can be well defined via the difference between two optical paths, even if the wavelength of two pulses are different by orders of magnitude. This robust condition allows almost all traditional techniques to become time-resolved measurements. Therefore, the probing energy scale is chosen according to the materials' electronic structure and the origin of response we want to investigate [1,2].

Charge-carrier's response is essentially important in semiconductors and can be very different in various materials, depending on external conditions like temperature and applied field, and internal properties such as crystal structure, electronic structure and electron-phonon coupling strength [2-4]. The common characteristic of carriers is that they distinctively respond to very low-frequency electromagnetic waves, typically of frequency 0.1-10s terahertz (THz), where $1 \text{ THz} = 10^{12} \text{ Hz} = 300 \mu\text{m} = 33.3 \text{ cm}^{-1} = 4.1 \text{ meV}$ [5]. Many electronic properties, namely, carriers momentum randomization [6], intra-excitonic transitions [7,8] and ultrafast electron-hole plasma buildup [9], can be resolved from the dielectric response in THz range (meV energy scale) [4,5]. Therefore, the problem becomes one of obtaining the dielectric response function, and theoretically, how to extract physical parameters via proper theoretical models [4,10].

Traditionally, meV energy scale radiations can be utilized to probe materials using Fourier-transform infrared spectroscopy (FTIR), which is only sensitive to the intensity (amplitude) of the IR light. This means that the Kramers-Kronig relations must be used to obtain the complex optical parameters, such as complex refractive index $\tilde{n}(\omega) = n(\omega) + \kappa(\omega)$ or complex optical conductivity $\tilde{\sigma}(\omega)$ or complex dielectric function $\tilde{\epsilon}(\omega)$ [11]. Due to the development of ultrafast techniques, THz time-domain spectroscopy (THz-TDS) based on sub-picosecond (sub-ps) laser pulses becomes a powerful technique [5]. By measuring the attenuation and delay of the THz pulse by the sample, one can extract $\tilde{n}(\omega)$ and hence $\tilde{\sigma}(\omega)$ or $\tilde{\epsilon}(\omega)$. If we now add a pump arm to first photoexcite the samples, we get time-resolved terahertz

spectroscopy (TRTS), where we now obtain the photoinduced change in complex optical conductivity (or photoconductivity) of the material in an ultrafast time scale [4].

Organometallic lead halide perovskites have become a star material in the past eight years, due to their outstanding photovoltaic performance. The highest certified record for perovskite solar cells is a power conversion efficiency (PCE) of 22.7% [12], which promises great potential of this material family as next-generation photovoltaics. After much research, researchers have now reached a consensus on the reasons for the large PCE, such as strong solar absorption, shallow levels arising from intrinsic defects and long-range balanced electron and hole diffusion lengths [13]. The carrier dynamics are the results of many complex microscopic transport processes, such as coupling with phonons [14], scattering with defects [13] and ion impurities [15].

Also, in the lead halide perovskites, the lowest-lying optical phonon modes are located in the THz range [16–20]. This enables us to use THz pulses to probe the carriers and phonon modes simultaneously, often with photoexcitation for the elucidation of the photophysics behind the outstanding photovoltaic performances.

1.2 Outline of the thesis

This thesis studies the carrier and phonon dynamics in various halide perovskite systems using THz-TDS and TRTS. The thesis is organized as follows:

- Chapter 2. The basic principles of THz generation and detection, THz-TDS and TRTS setups and the relevant data analysis procedures are introduced.
- Chapter 3. A brief history of perovskite solar cells and physical properties of lead halide perovskites is given. One concern, the stability issue, is briefly described.
- Chapter 4. $\text{CH}_3\text{NH}_3\text{PbBr}_3$ thin films are studied by THz-TDS, revealing the low-frequency transverse optical (TO)-phonon modes evolution with temperature. TO phonon mode splitting is observed near 150 K, which we attribute to the tetragonal–orthorhombic phase transition, which agrees well with DFT-based

lattice-dynamics simulations of the THz spectra. Two lowest-lying longitudinal optical (LO)-phonon modes are identified at 300 K. Room temperature carrier mobility is estimated using Feynman's polaron theory.

- Chapter 5. Mixed-cation perovskite thin films, $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$, are studied by THz-TDS and TRTS, revealing manifestations of carrier-phonon coupling. In our data we correlate changes in carrier scattering rate, carrier-LO phonon scattering channels and spectral weight changes of the carriers and phonon modes all together. Phonon-assisted exciton dissociation and photo-enhanced carrier screening ensure a large and long-lived free-carrier population in the system, especially at room temperature.

- Chapter 6. Sample-processing-method dependent study is conducted using TRTS to provide a deeper understanding of the difference of the photovoltaic performances. Organic ligand treated and pristine $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films are studied by TRTS. Ultrafast carrier dynamics and transport properties are studied comparatively.

- Chapter 7. Light and vacuum stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films is studied using THz-TDS, SEM and XRD. A home-made LED array is employed to investigate light stability of one-step grown samples in low humidity and under vacuum.

- Chapter 8. Main results of this thesis are summarized.

- Chapter 9. Future work.

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Chapter 2

Experimental Techniques and Data Analysis Methods

In this chapter, ultrafast terahertz spectroscopy techniques and relevant data analysis procedures used in this thesis are described. The chapter contains four parts: (1) terahertz time-domain spectroscopy, (2) time-resolved terahertz spectroscopy, (3) system calibration before ultrafast terahertz spectroscopy and (4) General data analysis procedures.

2.1 Terahertz time-domain spectroscopy

Terahertz time-domain spectroscopy (THz-TDS) is a coherent free-space time-gated technique. A “coherent” optical system is able to perform “coherent detection”, which means that an optical receiver can track the phase of a signal (and hence “phase coherence”). The “time-gated” detection (one type of coherent detection) is characterized by its capability to provide a time window so that a particular part of signal will be selectively detected in the time domain. In contrast to other frequency-resolved spectroscopic techniques, THz-TDS can directly measure the complex electric field $\tilde{E}(\omega)$ including both the amplitude and the phase. [1, 2] By comparing the THz electric field passing through two identical apertures, one with and the other without the sample, both attenuation and delay (and therefore the

refractive index and the absorption coefficient) can be determined without resorting to the Kramers-Kronig relations. [3]

THz-TDS has several other advantages over incoherent techniques, such as: (1) the ability of cutting off the Fabry-Perot reflections by using thick substrates and windowing the time-domain data; [*Fabry-Perot reflections are multiple reflections occurring on either side of a parallel-sided plate. *The operation of “windowing” data is to replace a rectangular function (equivalent, mathematically, to multiply the time-domain data by a temporal rectangular function) with an appropriate function to minimize the deviation between the windowed data and the real signal. [4]] (2) a contact-free manner, without the need to fabricate electrodes, to probe the free carrier response of a sample on a picosecond time scale; (3) the ability of extracting the complex optical properties of a sample without the need of the Kramers-Kronig transformation.

Of course, there are a number of disadvantages, such as: (i) the frequency range of THz-TDS is not as broad as that of traditional infrared technique, Fourier-transform infrared spectroscopy (FTIR), which is typically from several milli-electronvolt (meV) to several eV (several THz to 100s THz); (ii) in transmission geometry, for thin-film samples, the sample thickness needs to be within the proper range so that the transmission is neither close to zero nor one.

2.1.1 Terahertz generation and detection

Broadband THz sources are typically based on the conversion of ultrafast optical pulses into single-cycle THz pulses. For THz sources based on ultrafast optical pulses, coherent detection methods, based on optical sampling, are common solutions. Two widely used THz generation and detection schemes are based on photoconductive antennas or based on nonlinear media. [3, 5]

Based on photoconductive antenna The photoconductive (PC) antenna is one of the most frequently used devices for THz generation and detection. Figure. 2.1

shows the schematic diagram for PC-antenna based THz generation and detection. The PC antenna for THz generation or detection is made of two metal electrodes deposited on a semiconductor substrate. When a voltage is applied across the electrodes, electric energy is stored in the semiconducting gap area. The ultrafast laser pulse acts like a transient switch to trigger the reservoir of electric energy and release the excited carriers to be accelerated. The sub-ps-varying current is a source of THz electromagnetic radiations via $J(t) = N(t)e\mu E_b$, and $E_{THz} \propto \partial J(t)/\partial t$, where $J(t)$ is the photocurrent, $N(t)$ the density of free carriers, e the elementary charge, μ electron mobility, E_b the bias electric field and E_{THz} the generated THz electric field.

Figure 2.1: Schematic diagrams for PC-antenna based THz (a) generation and (b) detection. The difference between the THz generation and detection is the presence (absence) of a bias voltage in the THz generation (detection) setup.

In turn, without applying a bias across two electrodes, a PC antenna can be used to detect THz electric field by measuring photocurrent. Similarly, a laser pulse is absorbed by the semiconductor substrate, generating electron-hole pairs. Free carriers are accelerated by the THz electric field, E_{THz} , before they are recombined. As a result, a transient current is generated, $J(t) = \int_{-\infty}^t E_{THz}(t')\sigma(t-t')dt'$, hence $\tilde{J}(\omega) = \tilde{\sigma}(\omega)\tilde{E}_{THz}(\omega)$. We can see that the measured current is proportional to the THz electric field. Therefore, the THz electric field waveform can be mapped out by sampling at a set of time delays t_{THz} .

Based on non-centrosymmetric crystals For non-centrosymmetric crystals, a field at optical frequencies gives rise to a static electric field, which is recognized as optical rectification. If we assume the temporal profile of the laser pulse is Gaussian shape, $E(t) \sim E_0 e^{-at^2} e^{i\omega t}$, the optical-induced polarization P can be expressed as, $|P| \propto E_0^2 e^{-2at^2}$, where E_0 is the amplitude of laser electric field and ω is the frequency of the laser pulse. The induced polarization is proportional to the envelope of the femtosecond pulse. The schematic diagram is shown in Fig. 2.2.

Figure 2.2: Schematic diagram for optical rectification. The femtosecond pulse (dotted line) propagates from the left and through the nonlinear (NL) crystal. In the nonlinear medium, the induced polarization (solid line) gives rise to a THz electric field (dashed line). Taken from Ref. [5].

This induced polarization is varying with time, which is the source of the THz radiation, which can be understood by deriving Maxwells equations with a driving polarization term,

$$\nabla^2 E_{THz} - \frac{n_{THz}^2}{c^2} \frac{\partial^2 E_{THz}}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 P^{(2)}}{\partial t^2}, \quad (2.1)$$

where n_{THz} the refractive index of THz pulse in the nonlinear medium, c the speed of light in vacuum, ϵ_0 the vacuum permittivity and $P^{(2)}$ the second order term of polarization.

There are two reasons leading to efficient generation of THz pulses with sub-100

fs laser pulses: (1) nonlinear effects usually require high photon density in both temporally and spatially, and (2) the sub-picosecond laser pulse has a bandwidth as broad as several-to-tens THz.

Figure 2.3: THz detection scheme using nonlinear crystals. Before reaching EO crystal, the detection laser beam is with linear polarization. Without THz field: after a quarter wave plate, the beam is circular polarization, in which intensities in x and y directions are equal. With THz field: becoming elliptical polarization after $\lambda/4$, which gives a non-zero result. Taken from Ref. [5].

Detection of THz radiation using nonlinear crystals takes advantage of the Pockel's effect: when a quasi-static electric field is applied to an electro-optical (EO) crystal, it induces a change in the polarization of radiation passing through it. Figure. 2.3 shows the schematic diagram of THz detection using EO crystal.

Pockel's effect is the inverse effect of optical rectification. As a consequence, the non-centrosymmetric crystal shows a field-induced birefringence that the induced polarization is orthogonal to the optical and THz fields. Moreover, since the femtosecond pulse is much shorter compared to the THz pulse, the induced change in polarization is effectively proportional to the instantaneous value of the THz field (E_{THz}), which overlaps in time with the femtosecond pulse. Hence, the signal collection hereafter is polarization detection process. The balanced photodiodes are used to measure the difference between the intensities of two beams with the x - and y -direction polarizations, respectively, and the difference is proportional to the instantaneous THz electric field.

2.1.2 Terahertz time-domain spectroscopy setup

In this thesis, all THz-TDS measurements are finished with a commercial THz spectrometer (TeraView TPS 3000), combined with a Janis ST-100-FTIR continuous flow cryostat and a home-made three-axis alignment stage. Both THz generation and detection in TeraView TPS 3000 is based on PC antennas, combined with an 800-nm-centre-frequency oscillator (Coherent Vitesse). Figure 2.4b shows a typical THz-TDS setup schematic diagram. A sub-100 fs beam is divided into two: one laser pulse going to the THz source; the other pulse passes through an adjustable delay t_{THz} and overlap temporally and spatially with the THz pulse at the PC receiver. [6]

Figure 2.4: (a) Photograph and (b) schematic diagram of a commercial TPS spectra 3000. Taken from Ref. [6].

2.2 Time-resolved terahertz spectroscopy

The home-built time-resolved terahertz spectroscopy (TRTS) setup is based on a regenerative amplifier (800 nm, 40 fs, 1 kHz, Coherent Legend Elite amplifier seeded by a Coherent Mantis oscillator). The optical parametric amplifier (OPA) generate photons with a wavelength range from 400 nm to 1600 nm (Coherent TOPAS-prime). In the 1-kHz repetition rate of Legend laser system, the near-infrared pulse energy is as high as 3.5 mJ.

As an extension of THz-TDS, the setup of TRTS needs the laser beam split into two, one of which is as a pump beam, the other one, for a THz-TDS system, will be

further split into THz generation beam and the detection beam. A typical TRTS setup is shown in Figure 2.5. Two choppers, mechanically switching on / off with user-defined frequencies, are used in a TRTS system to modulate the THz pulses with chopping frequency of f_{THz} and optical pump pulses with chopping frequency of f_{pp} , simultaneously send f_{THz} and f_{pp} to two Lock-in amplifiers as the reference inputs, respectively. A polarizer is to clean the polarization of the detection pulse before overlap with the THz pulse. Compared with static THz-TDS, TRTS can measure the photoinduced change as a function of pump-probe delay t_{pp} from sub-ps to nanosecond (ns) time scale. As there are two delay lines t_{pp} and t_{THz} in TRTS, two experimental schemes are developed, namely, one-dimensional (1D) TRTS, two-dimensional (2D) TRTS.

Figure 2.5: A typical TRTS setup. BS, beam splitter; P, polarizer; $\lambda/4$, quarter wave plate; WP, Wollaston prism. Chopper 1 with frequency f_{THz} and chopper 2 with frequency f_{pp} are for static data and photoinduced changes acquisition, respectively. Due to two choppers in this setup, there are two lock-in amplifiers using the corresponding chopping frequency as the reference, to extract static data and photoinduced changes from the signal taken from the balanced photodiodes. Taken from Ref. [7].

1D-TRTS is also known as frequency-integrated time-resolved THz spectroscopy. In 1D-TRTS, detection laser pulse is kept at the THz pulse peak. Therefore time-resolved THz peak response is obtained by scanning t_{pp} . There is one obvious

drawback for 1D-TRTS: photoinduced change in both amplitude and phase can lead to 1D-TRTS signal change. This is due to the advantage of THz-TDS — the measured THz waveform is THz electric field — consisting of both the amplitude and phase of various frequency components. As a consequence, 1D-TRTS result is physically meaningful, from the transient terahertz absorption view, only when there is no photoinduced THz pulse distortion in the sample. If one cannot rule out of the THz pulse distortion in the sample, frequency-resolved TRTS is necessarily employed.

The aim of 2D-TRTS is to achieve the full advantage of time-gated technique. In 2D-TRTS, two choppers are used in the paths of THz generation (f_{THz}) and pump (f_{pp}), respectively. Two chopper controllers are synchronized with the repetition rate (1 kHz) from the TTL output of a Ti:Sapphire laser, so that choppers are coherently controlled by the laser. The sub-harmonic of chopper 1 and chopper 2 are set as 2 and 4, respectively, therefore, f_{THz} and f_{pp} are 500 Hz and 250 Hz, respectively. The signal will be double-modulated by these two frequencies, and can be extracted from two Lock-in amplifiers via referenced by 500 Hz and 250 Hz, respectively. Four kinds of signals will be detected in series, namely, (1) THz on-pump on, (2) THz off-pump on, (3) THz on-pump off and (4) THz off-pump off. Under this scheme, both the THz electric field passed through the sample $E_{t_{pp}}(t_{THz})$ and photoinduced change $\Delta E_{t_{pp}}(t_{THz})$ are measured simultaneously. Usually, a set of time delays $t_{pp,n}$ are preset according to 1D-TRTS. At each pump-probe time delay $t_{pp,n}$, scanning t_{THz} to take both $E_{t_{pp,n}}(t_{THz})$ and $\Delta E_{t_{pp,n}}(t_{THz})$, and then to do further analysis.

2.3 System calibration for THz-TDS/TRTS

THz beam diameter THz beam diameter is a very important parameter in both THz-TDS and TRTS. Since $1 \text{ THz} = 0.33 \text{ mm}$, at the focal point (sample position), the THz beam diameter can be as large as several millimeters.

Due to THz radiations can be totally absorbed/reflected by metal, a steel blade moving along z -direction is suitable to measure the diameter of a THz beam, as

Figure 2.6: (a) Spatial distribution of the THz field. (b) By moving a blade along z-axis, the THz electric field can be measured as a function of the blade vertical position. (c) Normalized THz electric field as a function of z -axis position.

shown in Fig. 2.6. The diameter is defined as the distance between 10% and 90% of the normalized THz peak signal. From Fig. 2.6c, we can see that the THz beam diameter at the focus is 1.83 mm.

Vaccum-to-vacuum measurements To obtain the THz transmittance $\tilde{T}(\omega) = \tilde{E}_{sam}(\omega)/\tilde{E}_{ref}(\omega)$, time-domain waveforms of the sample $\tilde{E}_{sam}(t_{THz})$ and reference $\tilde{E}_{ref}(t_{THz})$ must be measured separately.

Figure 2.7: Schematic diagrams of the sample holder in (a) the reference scan and (b) the sample scan. (c) Side view of the sample holder, and its geometric relations with the sample and substrates.

In the transmission geometry THz-TDS, each measurement includes two scans: measured THz pulse for the reference scan (passed through a bare substrate, blue

waveform in Fig. 2.7a) and for the sample scan (passed through the sample deposited on a substrate, red waveform in Fig. 2.7b). Since the laser as well as the electronics have their intrinsic instability, namely, noise and drifts, the THz system itself has a systematic instability. Therefore, before measuring the sample, the THz system must be calibrated to ensure that the significant distortion in THz waveform is mainly due to the sample rather from the system itself.

A home-made sample holder and a typical measurement schematic diagrams are shown in Fig. 2.7 for THz-TDS/TRTS. Two holes in the sample holder should be identical, to ensure the same amount THz radiation blocked. The movement in the z direction of the sample holder is controlled by a motorized stage mounted in a cryostat with an accuracy in distance of $2.5 \mu\text{m}$. We also need to try our best to make sure the THz beam passes through the center of both the hole for the sample (upper) and the hole for the reference (lower). Therefore, stages in x - y plane are needed.

Figure 2.8: A typical THz electric field transmittance in a vac-vac measurement.

In the system calibration, the transmittance of both holes filled with vacuum (vac-vac) is measured. Ideally, the transmittance of vac-vac should be unity and frequency-independent, with deviations from unity due to (1) laser instability, (2) the diameters of two holes are not exactly identical, (3) THz beam does not pass through exact center of the apertures, (4) apertures are not in the THz focal plane and (5) the z -stage does not move perpendicularly with the THz beam. A typical

transmittance of vac-vac is shown in Fig. 2.8. We note that there are wiggles within 0.2% from the unity in the amplitude of the vac-vac transmittance. According to this acceptable fluctuation range, we can identify the trustable frequency window in THz-TDS/TRTS measurements, for example, the trustable window in Fig. 2.8 is 0.3–2.8 THz. This 0.2% frequency-independent deviation from unity is, to the best of our knowledge, one of the best in the world for THz-TDS.

2.4 Data analysis procedures

Data analysis procedures for THz-TDS and 2D-TRTS are different, as the double-modulation technique in TRTS involves two data channels from the same signal source.

THz-TDS data analysis procedures The method for the THz-TDS data acquisition and analysis is illustrated with a flow chart shown in Figure 2.9.

In a transmission geometry THz-TDS, the transmitted temporal THz waveforms of both sample $E_{sam}(t_{THz})$ and reference $E_{ref}(t_{THz})$ are measured (Fig. 2.9a). Through Fourier transform, temporal THz waveforms are transformed into the frequency domain as complex electric fields $\tilde{E}_{sam}(\omega)$ and $\tilde{E}_{ref}(\omega)$ (the amplitude and the phase are shown in Fig. 2.9b and Fig. 2.9c, respectively). The complex transmittance $\tilde{T}(\omega)$ is obtained by dividing the complex sample field by the complex reference field, $\tilde{T}(\omega) = \tilde{E}_{sam}(\omega)/\tilde{E}_{ref}(\omega)$ (the amplitude and the phase are shown in Fig. 2.9d and Fig. 2.9e, respectively). The complex transmittance $\tilde{T}(\omega)$ can be expressed as a function of the complex refractive index $\tilde{n}(\omega)$ of all the THz transparent media during the experiment, including index of the sample and the substrate. Given the complex refractive index of the substrate, the frequency dependent complex refractive index $\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$ (Fig. 2.9f,g) can be extracted numerically.

Once the complex refractive index of the sample is obtained, subsequently optical parameters are derived, such as permittivity $\tilde{\epsilon}(\omega)$, conductivity $\tilde{\sigma}(\omega)$ and longitudinal response function $1/\tilde{\epsilon}(\omega)$. The complex conductivity $\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$

Figure 2.9: Data analysis procedures for THz-TDS, from (a) raw data (time-domain THz waveforms $E_{sam}(t_{THz})$ and $E_{ref}(t_{THz})$) through Fourier transform to the transmitted electric fields in frequency domain, including (b) the amplitude and (c) the phase. (d)&(e) The complex transmittance is a function of (f)&(g) the sample's refractive index. (h)&(i) Finally, the complex optical conductivity is derived from the obtained sample's refractive index. The subscripts “sam” and “ref” in the left hand side flow chart represent sample and reference, respectively.

(Fig. 2.9h,i) is obtained from the relation $\tilde{\sigma}(\omega) = i\omega\epsilon_0[1 - \tilde{n}(\omega)^2]$, where $\tilde{n}(\omega) = n(\omega) + i\kappa(\omega) = \sqrt{\tilde{\epsilon}(\omega)}$ [8].

2D-TRTS data analysis procedures The foremost aim in 2D-TRTS is to extract the photoinduced changes in the sample as a function of pump-probe delay. Usually, the photoinduced changes are relatively small compared with the static response. In some cases, the photoinduced changes are even on the same order of magnitude as the noise level, which requires the second modulation on the pump

beam.

Figure 2.10: Data analysis procedures for TRTS. (a) Pump-probe delays are selected from 1D-TRTS, before 2D-TRTS measurements. Red dots are selected points according to the rate of change in $-\Delta E/E$. Typically, at the earlier time after the excitation is, the more dense the time points are selected, due to the rate of change in $-\Delta E/E$. Inset: Zooming in the first 100 ps. A time delay, $t_{pp,static} < 0$, is selected for measuring the sample response in equilibrium. (b)&(c) Extracting complex conductivity in equilibrium. (d)&(e) Extracting complex conductivity at $t_{pp,m}$. (f)&(g) Photoconductivity at $t_{pp,m}$ is obtained by subtracting the conductivity in equilibrium from the conductivity at $t_{pp,m}$.

Firstly, the zero in the pump-probe delay is defined as time delay of the first non-zero data point in $-\Delta E/E$ (significantly larger than the noise level). A set of pump-probe delays, $t_{pp,static}, t_{pp,1}, \dots, t_{pp,m}, \dots, t_{pp,M}$ ($m = 1, 2, \dots, M$), are selected from 1D-TRTS scan (red dots in Fig. 2.10a). From Fig. 2.10a, in general, these time delays are chosen according to the rate of change in $-\Delta E/E$: the greater the change is, the more dense the time points are.

Secondly, at a negative pump-probe delay $t_{pp,static}$, both THz-TDS scans for the sample E_{static}^{sam} and the reference E_{static}^{ref} (Fig. 2.10b) are taken from the lock-in amplifier referenced by 500 Hz to analyze the sample response in equilibrium. Data

analysis procedures for the sample in equilibrium is same as that of THz-TDS. The complex conductivity $\tilde{\sigma}_{static}(\omega) = \sigma_{1,static}(\omega) + i\sigma_{2,static}(\omega)$ (Fig. 2.10c) is obtained.

Next, at a certain delay $t_{pp,m}$, photoinduced change in THz waveform $\Delta E_{t_{pp,m}}^{sam}$ (dashed green line in Fig. 2.10d) is taken from the Lock-in amplifier referenced by 250 Hz. The term $\Delta E_{t_{pp,m}}^{sam}$ is the change in the sample between pump on and pump off, therefore the actual response of the sample at $t_{pp,m}$ is $E_{t_{pp,m}}^{sam} = E_{static}^{sam} + \Delta E_{t_{pp,m}}^{sam}$. By employing the THz-TDS data analysis methods, the complex conductivity at time delay $t_{pp,m}$, $\tilde{\sigma}_{t_{pp,m}}(\omega) = \sigma_{1,t_{pp,m}}(\omega) + i\sigma_{2,t_{pp,m}}(\omega)$ (Fig. 2.10e), is therefore obtained.

Finally, the photoinduced change in complex conductivity $\Delta\tilde{\sigma}_{t_{pp,m}}(\omega)$ (Fig. 2.10g), is obtained by subtracting the conductivity in equilibrium (Fig. 2.10f), $\Delta\tilde{\sigma}_{t_{pp,m}}(\omega) = \tilde{\sigma}_{t_{pp,m}}(\omega) - \tilde{\sigma}_{static}(\omega)$.

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Chapter 3

Overview of Organometallic Lead Halide Perovskites

In this chapter, a brief history of perovskite solar cells and their properties will be given. It contains three parts: (1) a brief history of perovskite solar cells, (2) transport and optical properties of lead halide perovskites and (3) the stability issue.

3.1 A brief history of perovskite solar cells

The perovskite structure ABX_3 Historically, the perovskite structure is very common in inorganic crystals. Its chemical formula is ABX_3 , where A^{2+} and B^{4+} represent two different cations, and X^{2-} refers to the anions. Due to the interplay of the charge, spin and lattice degrees of freedom, there are many well-known inorganic perovskites with various novel properties, such as ferroelectricity, e.g. $BaTiO_3$, high- T_c superconductivity, e.g. $YBa_2Cu_3O_7$, ferromagnetism, e.g. $SrRuO_3$, colossal magnetoresistance (CMR), e.g. $(La/Sr)MnO_3$, multiferroicity, e.g. $BaMnO_3$ and so on [1]. These traditional perovskites are oxide compounds.

The lead halide perovskites referred in this thesis are organic-inorganic hybrid compounds. The major difference from the conventional inorganic perovskites is

that the A^+ site is an organic cation. Fig. 3.1 shows the perovskite structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3).

Figure 3.1: An example of perovskite structure: $\text{CH}_3\text{NH}_3\text{PbI}_3$. Taken from Ref. [2].

Solar energy has been widely used in human history. Compared with unrenewable fossil energy, solar power would yield an endless energy supply. In recent decades, solar energy has been the promising renewable energy candidate, through generating electricity from solar illumination by solar cells, to replace fossil energy. To achieve this aim, commercial solar cells must be fabricated and used on a large scale. It is necessary to cut down the cost of generating electricity from solar energy by either reducing the cost of processing procedures of photovoltaic (PV) devices or by enhancing the power conversion efficiencies (PCEs). [3, 4]. The PCE of a solar cell, is the percentage of the solar energy shining on a PV device that is converted into usable electricity [5]. Up to now, PCEs of solar cells based on inorganic semiconductors, such as Silicon and GaAs, have reached over 20% (Fig. 3.2) [6].

Dye-sensitized solar cells (DSSCs) have been demonstrated to be a potential candidate for the next generation technologies in PVs [7]. In contrast to traditional inorganic semiconductor-based solar cells, dye molecules are involved in photoelectrochemical processes in DSSCs. The sensitizer is photoexcited followed by electron injection into the conduction band of the mesoporous oxide semiconductor (for example, TiO_2), and regenerated by the redox system [8]. Since many dye

Figure 3.2: Efficiency chart for major solar cells from National renewable energy laboratory (Oct, 2017). The red circle highlights the fast rise in the efficiency of perovskite solar cells. Taken from Ref. [6].

materials can be selected, together with their low cost and easy fabrication, DSSCs meet the requirements of commercialization. In 2009, the organo-metallic tri-halide perovskites, MAPbBr_3 and MAPbI_3 , was utilized as the sensitizer in the DSSC with liquid electrolyte, with a PCE of 3.8% [9]. Three years later, for the first time, the perovskite MAPbI_2Cl was used as the light absorber with the solid-state mesoporous structure, which uses 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) instead of liquid electrolytes as the hole transport material [10]. This significant progresses triggered the development of all-solid-state perovskite solar cells (PSCs) until today, by avoiding the limitation of liquid electrolyte. This is significant for commercialized solar cells, because solid state devices save more space and they are to package by avoiding the issue of liquid electrolyte leakage. After several years of development, the PCEs of PSCs have

exceeded 20%, with the highest record of 22.7% [6]. High PCEs have approached those of commercialized Si-based solar cells (Fig. 3.2).

The layout of perovskite solar cells In 2009, the perovskite layer was a sensitizer in DSSCs, like other dye materials. These traditional PSCs were fabricated with solid-state mesoporous architecture, in which the mesoporous semiconducting metal oxides serve to collect the photo-generated charges from the perovskite layer (Fig. 3.3a). Later, it was found that PSCs without the mesoporous architecture worked as well. The stacked multi-layer structure (also known as planar heterojunction structure) was used in traditional thin-film solar cells, rather than in DSSCs due to the typically small diffusion lengths (the average distance that a carrier moves between generation and recombination) in dyes [4]. With the help of time-resolved techniques, researchers noted that in perovskite thin-film layers, not only could the charge carrier diffusion length reach 100s nanometers to 1 micrometer, but both electrons and holes showed this property [11, 12]. This efficient charge transport in perovskite films built the foundation for the subsequent development of highly-efficient planar heterojunction structural PSCs.

In the planar-heterojunction structure, perovskite film is the photo-absorber to generate both free electrons and holes. There are two layers that are in contact with this perovskite layer: one is the n-type electron transporting material (ETM) layer, and the other one is the p-type hole transporting material (HTM) layer, for selectively conducting the carriers to the relative electrodes as the opposite terminals of the devices. Initially, by imitating the architecture in DSSCs, the n-type layer was deposited before the perovskite layer, then the p-type layer was deposited after the perovskite layer. This architecture is defined as n-i-p structure (Fig. 3.3b).

The inverted structure design (Fig. 3.3c), in which deposition sequence is the p-type layer, the perovskite layer and finally the n-type layer (p-i-n structure), was adopted for organic photovoltaics (OPV) and later on applied to PSCs [4]. Figure 3.3d shows the schematic diagram of the working principle of inverted planar structure. Photo-generated electrons (holes) move to the ETM (HTM) layer due

Figure 3.3: Schematic diagrams of (a) mesoporous structure, (b) regular planar structure and (c) inverted planar structure. (d) Schematic diagram of the working principle of inverted planar structure. Taken from Ref. [4].

to the energy level design: the ETM (HTM) has a relatively low potential for conducting electrons (holes). These charge selective layers can reduce the energy barrier between perovskite film and electrode materials and suppress interfacial charge recombination.

All these adaptations in the PSCs taken from the DSSCs and OPVs, together with the physical properties described in Section 3.3 later, eventually enable the PSCs to overtake the DSSCs and OPVs in solar cell performance.

3.2 Physical properties of lead halide perovskites

Since 1989, lead-halide octahedron-based organic-inorganic hybrid perovskites have been systematically investigated that yielded many interesting structural, excitonic, optical and dielectric properties [13–16].

In chemical sciences, inorganic and organic compounds have fundamental differences. In inorganic crystals, the atoms are periodically aligned, and their properties

are better described by band structures. In contrast, most organic compounds do not possess long-range periodicity, so that the properties of organic compounds were described more like molecules with discrete energy levels rather than a crystal with continuous bands [17]. The MAPbX_3 ($X = \text{I}, \text{Br}, \text{Cl}$) perovskites consist of two sublattices consisting of an inorganic $[\text{PbX}_6]^{-4}$ octahedral framework and MA^+ organic cations. Due to these differences, there is a debate whether the hybrid nature (i.e. organic-inorganic) makes this perovskite family special [18].

First-principles calculations show that the density of states (DOS) near the band edge are dominated by the contributions of the inorganic framework [19, 20]. Figure 3.4 shows total density of states and MA^+ , Pb and I^- partial DOS.

Figure 3.4: Density-functional theory calculated DOS of MAPbI_3 . (a)–(d) are total DOS and MA^+ , Pb and I^- partial DOS, respectively. Taken from Ref. [20].

Moreover, the calculated bandgap showed the close matching with the experimental data, when spin-orbit coupling (SOC) was considered. Even *et al.* found that the SOC dramatically reduces the energy gap by affecting the conduction band [21]. Lee *et al.* employed first-principles calculations to attribute the origin of the tilt in inorganic halide frame to hydrogen bonding between an organic A-cation and the halide frame [22]. In the absence of the tilt, the bandgap would be very small, for example in MAPbI_3 , the bandgap was as small as 0.03 eV.

Strong solar absorption Figure 3.5 shows band structures of MAPbI₃ calculated by density-functional theory (DFT). In the tetragonal and the cubic phases, MAPbI₃ is a direct-bandgap semiconductor.

Figure 3.5: Band structures of (a) tetragonal and (b) cubic phase CH₃NH₃PbI₃, calculated by density-functional theory. Taken from Ref. [23].

The magnitude of bandgap is very important in PVs, according to Shockley–Queisser limit [24]. Shockley’s theory described a detailed balance limit on the efficiency–bandgap relations for single junction, which predicted a maximum efficiency of $\sim 30\%$ only when the bandgap (E_g) is located within the range of 1.0–1.5 eV. Under the assumption that the semiconductor absorbs a photon and generates one electron-hole pair, low-energy photons ($E_{\text{photon}} < E_g$) would not be absorbed. On the other hand, photons with a higher energy than the bandgap ($E_{\text{photon}} > E_g$) dissipates their excess energy via thermal relaxation channels. Note that the hot carrier relaxation processes do not contribute to the photocurrent [25], but only contribute to a temperature increase of the lattice. The bandgap of the absorber determines the open-circuit voltage V_{oc} upper limit of PV devices [25]. When the cell is operated at open circuit, the current is zero, and the voltage across the output terminals is defined as the open-circuit voltage. Remarkably, the PSCs has an absorbing perovskite layer as thin as only ~ 300 nm, yet they achieve an open circuit voltage as high as 1.07 V [26]. This performance is quite comparable to some of the best solar cells, namely, single-crystal GaAs and polycrystalline Cu(In,Ga)Se₂ thin-film solar cells, and better than those polycrystalline thin-film solar cells based

on CdTe and $\text{Cu}_2\text{ZnSn}(\text{Se,S})_4$ [27].

To evaluate the high optical absorption of lead halide perovskites, the optical absorption coefficient of MAPbI_3 was measured by De Wolf *et al.*, and compared with that of GaAs and crystalline silicon (*c*-Si) (Fig. 3.6) [28]. GaAs and *c*-Si was frequently compared, since GaAs-based cells hold the highest conversion efficiency among thin-film solar cells, while Si solar cells with efficiencies close to 20% currently dominate the photovoltaic market [6].

Figure 3.6: Absorption coefficient of $\text{CH}_3\text{NH}_3\text{PbI}_3$, GaAs and crystalline silicon at room temperature. Taken from Ref. [28].

Figure 3.6 shows that MAPbI_3 has a larger bandgap than GaAs and *c*-Si. The curve of the perovskite absorption coefficient shows a sharp shoulder near its bandgap, which is comparable with that of GaAs. Moreover, at photon energy of 1.6–2.6 eV, the absorption coefficient of MAPbI_3 is larger than that of GaAs, and more than one order of magnitude larger than that of *c*-Si. This high absorption coefficient with particularly sharp onset serves the strong solar absorption for MAPbI_3 .

Band-filling with free charge carriers Charge carrier recombination kinetics can be modelled by the rate equation [29],

$$-\frac{dn}{dt_{pp}} = k_1n + k_2n^2 + k_3n^3, \quad (3.1)$$

where n is the photogenerated carrier density, t_{pp} the time after photoexcitation, k_1 , k_2 and k_3 the first-, second- and third-order recombination rate constants, respectively. Charge carrier annihilation processes following photoexcitation can be: (1) first-order Shockley–Reed–Hall (trap-state-mediated) recombination; (2) second-order free carrier (electron–hole pair) recombination; (3) three-body Auger recombination (Fig. 3.7a–c) [29–31].

Figure 3.7: Three kinds of recombination schematic diagrams: (a) Shockley–Reed–Hall recombination, (b) electron–hole pair recombination and (c) Auger recombination. E_c , E_v and E_{trap} denote conduction band edge, valence band edge and trap states, respectively. Taken from Ref. [32].

In an excited semiconductor, one or more of these recombination mechanisms possibly exist. Through fitting the carrier density as a function of time with the rate equation, the actual mechanism(s), together with the rate constants, can be extracted.

Manser *et al.* investigated this issue with transient absorption (TA) spectroscopy, and found that the band-edge recombination follows second-order kinetics, indicating the dominant process is the recombination of free electrons and holes [33]. The absence of trap-mediated recombination is surprising, because usually low-temperature solution-processed thin films have a large number of trap states. However, at low carrier concentrations, there is non-negligible fraction of carrier recombination via the trap state-mediated pathway observed from time-resolved photoluminescence (TRPL) and 1D-TRTS [34]. Note that all techniques mentioned above have their limitations in probing carrier recombination kinetics: (1) TA is basically

probing the band filling through interband transitions, hence is sensitive to the change in complex refractive index; (2) TRPL only detects radiative combinations, not non-radiative ones; (3) THz electric field can be directly absorbed by free charge carriers, however 1D-TRTS is a frequency-integrated technique, which leads to the fact that one cannot disentangle the contribution of carrier concentration and scattering rate to the photoconductivity. A more careful study on MAPbI₃ was reported by La-o-vorakiat *et al.* using 2D-TRTS [35]. At all temperatures they studied, the first-order recombination has negligible contribution, while the second- or third-order process is dominant. However, under standard solar illumination condition (100 mW/cm²), third-order processes such as Auger process should be a minor effect. Therefore, under solar illumination, second-order processes dominate carrier recombination.

Small excitation binding energy Electron and hole quasiparticles can attract each other through mutual Coulomb interaction. The attractive interaction can lead to forming a bound electron-hole pair. This neutral bound pair is called an exciton. Figure 3.8 shows schematic diagram of free electrons and holes, and excitons. A minimum energy to dissociate an exciton into a free electron and a free hole is called exciton binding energy.

Figure 3.8: Schematic diagram of (a) free carriers and (b) exciton. Taken from Ref. [36].

Exciton binding energies of 37–50 meV (MAPbI₃ and MAPbBr₃) were deduced from magnetoabsorption spectroscopy measurements at liquid helium temperature [37,38]. D’Innocenzo *et al.* identified the exciton binding energy in the organo-lead mixed-halide perovskite to be 55 meV [39]. However, through measuring the magnetic field dependence of the optical density for the perovskite MAPbI₃, the

exciton binding energy was only 16 meV in the low-temperature orthorhombic phase, and a few meV in the tetragonal phase [40]. The authors attributed the difference to the use of low- ($\epsilon = 25.7$) or high- ($\epsilon = 5.6$) frequency dielectric constant, which has pointed out by several authors [41–43]. Initially, researchers used the small dielectric constant, by assuming energies of optical phonon modes are larger than exciton binding energy, because at that time, high quality Raman or THz results had not been reported. In practice there are many optical phonon modes with energy from 3 meV to 20 meV [44–47]. Now we know that free carriers, excitons and optical phonon modes response to THz electromagnetic radiation, in halide perovskites. Most probably, they couple with each other between any two of them. We will discuss TRTS results on the carrier–phonon coupling, together with exciton formation/dissociation in mixed-cation halide perovskite later in Chapter 5.

Balanced electron–hole diffusion lengths: long carrier lifetimes & high carrier mobility In the planar-heterojunction structure, several-hundred-nm-thick perovskite layer is localized at the middle. It is necessary that both photo-generated electrons and holes can transport to the relative carrier transporting material layers before annihilation. Therefore, balanced electron–hole diffusion lengths, diffusion length of electrons and holes are comparable, become a necessary condition.

Two-dimensional transient absorption microscopy imaging is shown in Fig. 3.9 [48]. Due to the unoccupied/occupied state filled by the diffusing carriers, carrier diffusion is represented by the evolution of the carrier distribution profile as a function of time. Through analyzing the experimental data with a diffusion model, a diffusion length of 1.2 μm over a lifetime of 50 ns was obtained.

La-o-vorakiat *et al.* obtained the free carrier mobility and carrier density dynamics simultaneously from their 2D-TRTS data, and defined diffusion length L_D as [35],

$$L_D(t_{pp}) = \sqrt{\frac{2D(t_{pp})}{k_{eff}}} = \sqrt{\frac{2\mu_{eff}k_BT/e}{-\frac{1}{n}\frac{dn}{dt_{pp}}}}, \quad (3.2)$$

where D is the diffusion constant at temperature T , t_{pp} the time after photoexcita-

Figure 3.9: Top: two-dimensional transient absorption microscopy imaging. The scale bar in the 2D imaging is $300 \mu\text{m}$. (a) One-dimension scan of excited-state density, and the profiles are fitted by Gaussian functions. (b) Diffusion coefficients obtained from fitting of Gaussian profiles in (a). Taken from Ref. [48]. (c) Diffusion lengths obtained from 2D-TRTS. Taken from Ref. [35].

tion, k_{eff} is the effective recombination rate constant, μ_{eff} is the effective mobility, e is the elementary charge and n is the carrier density. The diffusion lengths at 15, 80, 180 and 285 K are shown in Fig. 3.9c. This study confirmed the diffusion length was larger than $1 \mu\text{m}$ at room temperature. The diffusion length is much larger than the perovskite film thickness (typically 200–300 nm), so that photogenerated charge in perovskite thin films can be efficiently extracted before recombining.

The long diffusion length is a result of both long carrier lifetimes and high carrier mobility. The carrier lifetime can be as long as nanosecond-to-microsecond in MAPbI_3 single crystals [49].

Carrier mobility in halide perovskites are often described as high, compared to those of charge carriers in organic semiconductors [50]. Table 3.1 lists carrier mobilities for common PV materials at room temperature.

In polar semiconductors, carrier mobility is often limited by the scattering between carriers and the lowest-frequency optical phonon modes. The upper limit of carrier mobility thus can be obtained by using Feynman’s polaron theory [59]. Mobilities obtained from measurements on single-crystals (see Table 3.1) agree well with calculated carrier mobility values, which place an upper limit of $200 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at the room temperature [44, 45, 47]. The exact details of how these mobility values were obtained will be described in Chapter 4 later.

Table 3.1: Representative charge carrier mobilities for common PV materials at room temperature. ^aData are based on ref. [51]. ^bData are based on ref. [52]. ^cData are based on refs. [53–58].

Material	Mobility (cm ² V ⁻¹ s ⁻¹)	
	electron	hole
GaAs crystal ^a	~8000	~400
Si crystal ^a	~1500	~500
CdTe crystal ^a	≤~1000	≤~100
Organic crystal ^b	≤~0.1	≤~15
MAPbI ₃ and MAPbBr ₃ crystals ^c	≤~200	≤~200

Shallow trap states from intrinsic point defects As thin-film solar cells, point defects in the polycrystalline thin film should be numerous and unavoidable. Yin and co-authors performed pioneering point defect study on MAPbI₃ [20, 60].

A key result from this study is that a large majority of point defects exist as shallow states, which are energy levels lies very near to the valance band (VB) and conduction band (CB) edges.

Figure 3.10 shows point-defect levels of various tpyes of point defects in MAPbI₃. The acceptors / donors are ordered by the formation energies (shown in parentheses in Fig. 3.10 from left to right). Note that defect levels (both acceptors and donors), with a smallest formation energy, are shallow states.

This unique property of halide perovskites is a possible origin of their superior solar cell performance. The shallow trap states ensure that the open circuit voltage in perovskite solar cells is as high as 1.07 V, rather than suffer significant voltage loss due to the deep trap levels. Moreover, trapped charges near the conduction band minimum or the valence band maximum can be easily dissociated via inelastic scattering with other free carriers or *with low-lying phonons*. This makes possible the escape of the charge carriers from these trap states, even for carriers that have relaxed to the bottom of the CB. Later in Chapter 5, our TRTS work on mixed halide-alloyed formamidinium perovskites shows the contribution of these low-lying phonons, playing an important role on phonon-assisted exciton dissociation and carrier relaxation.

Figure 3.10: Calculated various types of point-defect levels in MAPbI₃. The intrinsic point defects are: I, MA and Pb interstitials (I_i , MA_i and Pb_i); I, MA and Pb vacancies (V_I , V_{MA} and V_{Pb}); I atoms at MA sites (I_{MA}), I atoms at Pb sites (I_{Pb}), MA molecules on I sites (MA_I), MA molecules on Pb sites (MA_{Pb}), Pb atoms on I sites (Pb_I), and Pb atoms at MA sites (Pb_{MA}). The formation energies of neutral defects are shown in parentheses. Taken from Ref. [60].

3.3 Stability issue

One obvious drawback of PSCs is the poor stability against light and water [61–64]. In the NREL efficiency chart, PSCs are still labeled as “not stabilized” (Fig. 3.2) [6]. As known [3], the longer the life of the device is, the less the cost is. More importantly, this poor stability causes unreliability. Therefore, this drawback is deadly.

Stability studies on lead halide have been done under various conditions, such as moisture [65] and ultraviolet (UV) light [66]. Figure 3.11a shows UV–visible spectra of MAPbI₃ as a function of time for perovskite films exposed to relative humidity (RH) = $(98 \pm 2)\%$ at $(22.9 \pm 0.5)^\circ\text{C}$. The rate of the degradation under various humidities is shown in Fig. 3.11b. MAPbI₃ films rapidly degrade in high humidity (RH $\geq 80\%$). Figure 3.11c shows the stability of mesoporous-TiO₂ based PSCs exposed to full solar (AM 1.5) irradiation. The encapsulated solar cells decay much faster than the non-encapsulated solar cells when exposed to full solar irradiation. This is later explained by the authors: surface adsorbed oxygen is desorbed upon UV illumination, forming the deep electronic trap sites [64]. These trap sites act as

Figure 3.11: (a) UV-vis spectra of MAPbI₃ film exposed to N₂ gas with RH = (98±2)%. (b) Time evolution of normalized absorbance at 410 nm, exposed to various RHs. (a)&(b) are taken from Ref. [65]. (c) Stability of mesoporous-TiO₂ based PSCs exposed to full solar (AM 1.5) irradiation with and without nitrogen encapsulation and exposure to UV light (using a 420 nm long pass filter). Taken from Ref. [66].

a rapid recombination pathway for carriers, resulting in a dramatic drop in charge collection efficiency. Encapsulated with nitrogen, the exposure to UV light strongly affect the performance of PSCs. Short-circuit current J_{sc} in Figure 3.11c is the current through the solar cell when the voltage across the solar cell is zero.

One method to improve the stability is through cation engineering [67]. The size of the cations should be suitable in a certain lead-halide framework. A suitably-sized cation can enhance the structural stability, hence the polycrystalline thin film stability.

Another good method is to make sure there is complete chemical reaction from the precursors to perovskites, during the sample fabrication process [68]. Some treatment schemes with nano-scale morphology control have been reported as candidates to solve this problem [69].

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Chapter 4

Low-Frequency Optical Phonon Modes and Carrier Mobility in the Halide Perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Using Terahertz Time-Domain Spectroscopy

In photovoltaic applications, the light absorber should have long and balanced diffusion lengths for both the photogenerated electrons and holes, which necessitates high carrier mobility. In polar semiconductors, the room-temperature carrier mobility is often limited by the scattering between carriers and the lowest-frequency optical phonon modes. In this work, we utilized terahertz time-domain spectroscopy to study the temperature evolution of low-lying optical phonon modes in $\text{CH}_3\text{NH}_3\text{PbBr}_3$. With the knowledge of these phonon modes, carrier mobility values can be predicted using Feynman's polaron theory. This method provides a way, from a fundamental physical view, to estimate the upper limit of carrier mobilities without the need to create photogenerated free carriers. This work has been published in Appl. Phys. Lett., 111:201903, 2017.

4.1 Introduction

In the very first paper that used both MAPbI₃ and MAPbBr₃ as light sensitizers, perovskite-based DSSCs have reached PCEs of 3.13% and 3.81%, respectively [1]. Interestingly, hole-transporter free perovskite/heterojunction solar cells can reach the PCE as high as 5.5% under the standard AM 1.5 solar light of 1000 W/m² intensity [2]. This means that the lead halide perovskites have high carrier mobility, so that the perovskite layer itself can be a hole transport layer.

Hybrid perovskites have been characterized by various experimental techniques including Raman spectroscopy [3], photoluminescence (PL) spectroscopy [4], transient-absorption (TA) spectroscopy [5], X-ray diffraction [6] and neutron scattering [7].

In the MAPbBr₃ polar crystals, free charge carriers are dressed by the phonon cloud as polarons [8]. It is therefore important to study the lowest-lying phonon modes and their evolution with temperature, in order to investigate the transport processes in these materials.

In MAPbX₃, the orthorhombic-to-tetragonal phase transition is accompanied by the MA⁺ cation orientation order-disorder behavior [9, 10]. The C–N axis is frozen in the orthorhombic phase, while the dipole has various possible orientations in the tetragonal and cubic phases [9].

The THz response of MAPbI₃ has been studied both theoretically and experimentally [10–12]. La-o-vorakiat *et al.* reported high-quality THz spectra of MAPbI₃ as a function of temperature [11]. Phonon modes splitting near the tetragonal-to-orthorhombic phase transition are observed using THz-TDS. They attributed this phonon mode (Pb–I bonds) splitting behavior to a lattice parameter change during the phase transition [13].

In contrast, the bromide analogue MAPbBr₃ has received relatively lesser attention, although the latter has been widely employed in mixed-cation and mixed-halide perovskites [14], to improve the stability of all-perovskite tandem cells. In single crystal, the structural phase transitions in single-crystal MAPbBr₃ are reported to take place at [9]:

Figure 4.1: Temperature dependent THz conductivities of MAPbI₃ thin films: (a) the real part $\sigma_1(\omega)$ and (b) the imaginary part $\sigma_2(\omega)$. Two phonon modes split into four near 150 K, due to the structural phase transition. The complex conductivities are modeled by Lorentzian oscillators. Taken from Ref. [11].

Figure 4.2: High-quality Raman spectra of MAPbBr₃ single crystals at 79, 155 and 295 K, corresponding to the crystal in the orthorhombic, tetragonal and cubic phases, respectively. Taken from Ref. [3].

Yaffe *et al.* reported low-frequency Raman spectra of MAPbBr₃ single crystals (Fig. 4.2) [3]. Frequency shifts in Raman spectra are attributed to the absorption/emission of Raman-activated phonon modes. Sharp, well-frequency-resolved Raman spectra are observed at 79 K, while at 155 and 293 K, resonance frequencies of

modes are not able to be identified from the broad features. We can see that these low-frequency phonon modes are located below 100 cm^{-1} (3 THz), which can be observed in a THz-TDS study on MAPbBr₃.

In this chapter, the temperature evolution of the low-lying optical phonon modes in MAPbBr₃ thin films is studied from 20 K to 300 K in the region of 0.3–2.8 THz. We observed that two peaks in the tetragonal and cubic phases split into three peaks in the orthorhombic phase, with the additional mode at 1.8 THz gradually appearing near the orthorhombic-to-tetragonal phase-transition temperature. By comparing THz-TDS results with first-principles density-functional theory (DFT) calculations, we attribute the phonon-mode splitting to the orthorhombic-to-tetragonal phase transition.

4.2 Sample precessing methods

The perovskite precursor solution was prepared by dissolving MABr and PbBr₂ in a stoichiometric ratio in dimethylformamide/dimethyl sulfoxide (4:1 v/v, 1 M) at 80 °C. The precursor solution was spin-coated onto a *z*-cut quartz substrate ($10\times 10\times 1$ mm) at 1000 rpm for 10 s and 4000 rpm for 30 s, with 250 μL of chlorobenzene being dripped onto the sample surface after 15 s during the second stage of the spin coating. Subsequently, the perovskite layer was annealed at 80 °C for 5 mins, and 100 °C for 10 mins. The MAPbBr₃ thin films were prepared by Mr. Hu Hongwei (MSE, NTU).

SEM measurements are shown in Fig. 4.3. From the measurements of thickness at multiple locations, we obtain sample thickness (932 ± 11) nm. The inset of Fig. 4.3 shows the photo of the sample. The sample was kept under nitrogen before being mounted onto our THz-TDS system under vacuum (10^{-7} mbar). This was maintained throughout the measurements to minimize exposure of the sample to air.

Figure 4.3: SEM micrograph of MAPbBr₃ film (cross section). Inset: the photo of the MAPbBr₃ sample. Taken from Ref. [15].

4.3 Experimental results

As dipole oscillators, the relative motions between cations and anions show Lorentzian behavior. At the resonant frequency, the dipole will strongly absorb the THz radiation, leading to an absorption peak in the real part of the optical conductivity $\sigma_1(\omega)$, and a rise up across zero in the imaginary part $\sigma_2(\omega)$ (Fig. 4.4).

4.3.1 TO phonon mode splitting

Two phonon modes are identified at 1.35 THz (mode 1) and 2.19 THz (mode 2) at 300 K, which mode 1 can be attributed to the buckling of Br–Pb–Br bond, and mode 2 to the changes in the length of the Pb–Br bond [16]. Above 150 K, two phonon modes are observed, while below 150 K, an additional mode at 1.8 THz gradually becomes a dominant peak at the lowest temperature (Fig. 4.4a). Note that 150 K is near the reported the tetragonal-to-orthorhombic phase transition temperature in single crystals, clearly indicating the structural phase transition induced phonon mode splitting. Additionally, three weak modes at 0.7, 1.0 and 2.6 THz can only be identified below 150 K. From the DFT calculations, we can see that multiple modes coexist around these central frequencies (Fig. 4.5a). Therefore, it is reasonable that

Figure 4.4: Temperature evolution of THz conductivities in thin-film MAPbBr₃: (a) real part $\sigma_1(\omega)$ and (b) imaginary part $\sigma_2(\omega)$. Partial contributions from individual Lorentzian oscillators (solid lines in purple and red) are plotted for $\sigma_1(\omega)$ at 20 K and 300 K. Two phonon modes (modes 1 and 2) are observed above and below 150 K, while one additional mode (mode 3) appears below 150 K due to the tetragonal–orthorhombic phase transition. The dashed arrow is pointing to the additional phonon mode 3. Taken from Ref. [15].

the phonon-mode splitting features appear around the structural phase transition temperature.

Temperature-dependent THz measurements have shown the fingerprints of structural phase transitions. To further confirm the shoulder/peak feature below 150 K is due to the tetragonal-to-orthorhombic phase transition, we compare our THz spectra with DFT-based lattice-dynamics simulations of the THz spectra by Dr. Jonathan M. Skelton (University of Bath) [16, 17]. In his calculations, the Γ -point phonon frequencies and eigenvectors and the atomic Born effective-charge tensors were then obtained using the density-functional perturbation theory, which were then combined to calculate the mode IR activities according to the method outlined in Skelton *et al.* [18].

From Fig. 4.5a, in the orthorhombic phase, we can see that the major features in both the experimental and simulated spectra are two major peaks (labelled 1 and 2) and one shoulder (labelled 3) between them. According to the simulated

Figure 4.5: Simulated THz spectra of MAPbBr₃ in the (a) orthorhombic and (b) cubic phases. By assuming a nominal 0.25 THz (orthorhombic phase) and 0.45 THz (cubic phase) linewidth for all the modes, simulated THz absorption spectra can be obtained (filled curves). In the orthorhombic phase, new phonon peaks appear between 1.5 and 2 THz, marked by an arrow in (a), in agreement with the experimental data (vertically-shifted solid lines). Taken from Ref. [15].

spectra, the shoulder results from two weak IR-active phonon modes in the 1.5–2 THz range which exist only in the orthorhombic phase. In the same spectra range, there are no mode in the cubic phase, which is in agreement with our measurements. Therefore, the lattice dynamic calculations support our experimental observation that the shoulder feature in the 1.5–2 THz range is present only in the orthorhombic phase.

Note that simulated spectra of MAPbBr₃ in both orthorhombic and cubic phases are blue-shifted to higher frequencies compared with our experimental measurements. Similar phenomena have been observed in the IR-active modes by Ahmed *et al.* in MAPbI₃ [19], and high-quality Raman spectra on single-crystal MAPbI₃ and MAPbBr₃ samples [3, 16]. These differences may be due to the fact that the DFT calculations treated the thermal 0 K structures — at non-zero Kelvin, which is the case for all measurements, the phonon modes shows softening and anharmonicity with increasing temperature. Another possible reason is, in hybrid organic-inorganic compounds, the calculations account the cation being frozen in one particular orientation in the cubic phase, although this may not be an issue for the simulated spectra in the orthorhombic phase.

We model the experimental spectra, $\tilde{\sigma}(\omega)$, using a set of Lorentz oscillators, with

two oscillators for spectra taken above 150 K, and three for those measured below 150 K:

$$\tilde{\sigma}(\omega) = -i\omega\epsilon_0(\epsilon_\infty - 1) + \sum_m \frac{\epsilon_0\omega_{p,m}^2\omega}{i(\omega_{TO,m}^2 - \omega^2) + \omega\gamma_m}, \quad (4.1)$$

where $\omega_{p,m}$, $\omega_{TO,m} = 2\pi f_m$ and γ_m are the oscillator strength, transverse optical (TO)-phonon frequency and linewidth of the m th oscillator, respectively. All dielectric contributions from beyond our experimental frequency window are accounted as high-frequency dielectric constant ϵ_∞ .

We noted that the phonon mode-splitting feature does not appear suddenly below 150 K. This is most likely the temperatures of the tetraII-to-ortho (148.8 K) and tetraI-to-tetraII (154.0 K) transitions are very close to each other and the transition temperature range can be as broad as ± 20 K in thin-film samples [20]. Therefore all three phases — ortho, tetraI and tetraII — coexist within the temperature range of 130–170 K. We do not observe any obvious signatures of structural phase transitions among the cubic, tetraI and tetraII phases in the conductivity spectra, which is probably due to the broadened linewidth by several equivalent orientations of C–N axis.

Figure 4.6a shows the temperature evolution of the oscillator strengths of modes 2 and 3. The combined oscillator strength of modes 2 and 3 is conserved near 140 K, indicating that the mode 2 splits into modes 2 and 3 from the tetraII phase into in the orthorhombic phase.

4.3.2 LO phonon modes

As an analogue of dielectric function $\epsilon_2(\omega)$, $\sigma_1(\omega)$ shows peaks at the TO phonon frequencies (ω_{TO}). In contrast, peaks in the loss function $-\text{Im}[1/\tilde{\epsilon}(\omega)]$ (which is the negative imaginary part of the complex response function $1/\tilde{\epsilon}(\omega)$) determine longitudinal optical (LO)-phonon mode frequencies ω_{LO} [21, 22].

The 300 K loss function data are shown in red circles in Fig. 4.6b. Since the upper frequency limit of our setup is 2.8 THz, only one peak can be identified at 1.59 THz, while another peak is located beyond our frequency window. Due to the high

Figure 4.6: (a) Evolution of oscillator strengths of mode 2 and 3 with temperature. The blue dashed line illustrates the combined oscillator strength of mode 2 and 3. The temperature range of 0–300 K is divided into four parts (top bar) by three reported phase transition temperatures. (b) The extrapolated (black solid) loss function $-\text{Im}[1/\epsilon(\omega)]$, calculated from the fitting parameters of $\tilde{\sigma}(\omega)$ at 300 K, with the loss function directly obtained from the experimental data (red circles). Taken from Ref. [15].

quality of spectra, the second peak can be obtained by using the fitting parameters obtained from the fit of 300 K complex conductivity $\tilde{\sigma}(\omega)$, and evaluating $\tilde{\sigma}(\omega)$ up to higher frequencies. Figure 4.6b shows the calculated loss function (black solid), showing two peaks at $\omega_{LO,1}/2\pi=1.59$ THz and $\omega_{LO,2}/2\pi=3.55$ THz.

Since the second peak position in the loss function is obtained from the simulation out of the experimental frequency range, we proceeded to check the consistency with the Cochran-Cowley relation [23]

$$\frac{\epsilon_{static}}{\epsilon_{\infty}} = \prod_{i=1}^2 \frac{\omega_{LO,i}^2}{\omega_{TO,i}^2} \quad (4.2)$$

where ϵ_{static} is the static dielectric constant. Taking $\epsilon_{static} \sim 25$ and $\epsilon_{\infty} = 6.7$ from Fig. 4.7, the two TO-phonon mode frequencies $\omega_{TO,1}/2\pi = 1.35$ THz and $\omega_{TO,2}/2\pi = 2.19$ THz from the conductivity data, and $\omega_{LO,1}/2\pi = 1.59$ THz, we calculate $\omega_{LO,2}/2\pi$ to be 3.59 THz — this value of $\omega_{LO,2}/2\pi$ is in excellent agreement with the value of 3.55 THz obtained from our loss function simulation spectra. Therefore, through the Cochran-Cowley relation, we have shown an independent confirmation of the accuracy of the two LO phonon mode frequencies.

In a previous published work, the second LO-phonon peak was observed at 5 THz

Figure 4.7: The real part of 300 K MAPbBr₃ dielectric function ϵ_1 . We take ϵ_1 at 0.3 THz as our ϵ_{static} (~ 25). Taken from Ref. [15].

by Sendner *et al.* [24], which differs from our 3.55 THz value. The possible origins for the discrepancy are discussed below. First, the real part of refractive index $n(\omega)$ depends very sensitively on the difference in thickness of the sample and reference substrates ΔL , which significantly affects the real part of dielectric function ϵ_1 , resulting in uncertainty in the peak positions in the loss function. We therefore measure ΔL with $\pm 0.1 \mu\text{m}$ resolution by a Mitutoyo micrometer. Five different positions on the substrate were measured for each substrate (see Fig. 4.8 for the measured positions and Table 4.1 for the standard deviation). We finally obtain $\Delta L = (4.0 \pm 0.5) \mu\text{m}$.

Figure 4.8: Five measured positions on the z -cut quartz ($10 \times 10 \times 1 \text{ mm}$). Taken from Ref. [15].

Second, from the measured value of ΔL , we plotted the loss function spectra $-\text{Im}[1/\tilde{\epsilon}(\omega)]$ in Fig. 4.9, for $\Delta L = 3.5, 4.0$ and $4.5 \mu\text{m}$ and $d = 932 \text{ nm}$. We see that both the oscillator strength and the phonon frequency of the second mode ($\omega_{LO,2}$) vary significantly. Fitting parameters $\omega_{LO,1}$, $\omega_{LO,2}$ and the corresponding ΔL are

Table 4.1: Measured thickness of z -cut quartz for the sample substrate (Sam.) and the reference substrate (Ref.) at positions shown in Fig. 4.8. Units are in μm .

Micrometer resolution		Position					Mean values	Standard errors	ΔL
		1	2	3	4	5			
0.1 μm	Ref.	952.9	953.8	954.0	951.9	952.2	953.0	0.4	4.0 ± 0.5
	Sam.	949.0	949.0	949.2	949.0	948.8	949.0	0.1	

summarized in Table 4.2. This procedure therefore enables us to obtain the standard error in both LO frequencies, and we finally get $\omega_{LO,1}/2\pi = (1.59 \pm 0.03)$ THz and $\omega_{LO,2}/2\pi = (3.55 \pm 0.48)$ THz.

Figure 4.9: Measurements (red squares) and simulation (black solid) with different ΔL . Taken from Ref. [15].

Table 4.2: Fitting parameters $\omega_{LO,1}$ and $\omega_{LO,2}$ are obtained with various values of ΔL .

Parameter	Lower-boundary	Mean value	Upper-boundary
ΔL (μm)	3.5	4.0	4.5
$\omega_{LO,1}/2\pi$ (THz)	1.56	1.59	1.62
$\omega_{LO,2}/2\pi$ (THz)	3.27	3.55	4.03

Finally, the complex response function $1/\tilde{\epsilon}(\omega)$ is simulated using $\Delta L = 4.0 \mu\text{m}$, $d = 932 \text{ nm}$, and fitted by two Lorentz oscillators,

$$\frac{1}{\tilde{\epsilon}(\omega)} = \sum_{i=1,2} \left[\frac{-W_{LO,i}^2}{\omega_{LO,i}^2 - \omega^2 - i\omega\gamma_{LO,i}} \right] + \frac{1}{\epsilon_\infty}, \quad (4.3)$$

to obtain the weight $W_{LO,i}^2$ and resonant frequency $\omega_{LO,i}$ for each LO mode: $(W_{LO,1}/2\pi)^2 = (1.65 \times 10^{-2}) \text{ THz}^2$, $\omega_{LO,1}/2\pi = 1.59 \text{ THz}$; $(W_{LO,2}/2\pi)^2 = (1.22) \text{ THz}^2$, $\omega_{LO,2}/2\pi =$

3.55 THz.

In the presence of multiple LO-phonon modes, such as MAPbBr₃, Hellwarth *et al.* derived an *effective* LO mode frequency $\omega_{LO,eff}$, accounting all scattering channels due to LO phonon modes into one effective mode [25]. Knowing the frequencies and weights of the individual modes, $\omega_{LO,eff}$ can be calculated via the relations: $\frac{W_{LO,eff}^2}{\omega_{LO,eff}^2} = \sum_i \frac{W_{LO,i}^2}{\omega_{LO,i}^2}$, and $W_{LO,eff}^2 = \sum_i W_{LO,i}^2$. From these two equations, we utilized

$$\omega_{LO,eff}^2 = \sum_i W_{LO,i}^2 / \sum_i \left(\frac{W_{LO,i}^2}{\omega_{LO,i}^2} \right), \quad (4.4)$$

to finally obtain $\omega_{LO,eff} = 3.46$ THz in MAPbBr₃.

Figure 4.10: The loss function of MAPbBr₃. Data below 15 THz are same as Fig. 4.9b; data above 15 THz are taken from Pérez-Osorio *et al.* [12]. This figure is taken from Ref. [15].

As we mentioned, carriers are scattered by all phonon modes in semiconductors, while in contrast, we only obtained two lowest-frequency modes. We next justify the validity of the use of this effective LO mode $\omega_{LO,eff}$ to calculate the carrier mobility. According to Eq. (4.4), the following two points are noted.

First, the sum in the denominator, $\sum_i \left(\frac{W_{LO,i}^2}{\omega_{LO,i}^2} \right)$, is dominated by the smallest values of $\omega_{LO,i}$, by assuming the same weight $W_{LO,i}^2$ for all modes. Therefore, the lowest-lying phonon mode frequencies determine $\omega_{LO,eff}$.

Second, in MAPbBr₃, the weight $W_{LO,i}^2$ is also dominated by the lowest-lying phonon modes — see Fig. 4.10. The weights of modes below 10 THz are much larger than those above 10 THz. As a result, contributions to $\omega_{LO,eff}$ from the

higher-frequency modes are negligible.

4.3.3 Calculated carrier mobility

As a light absorber in solar cells, high carrier mobility is always desirable at its working temperature. Measured carrier mobility as high as 10–100 cm²V⁻¹s⁻¹ have been reported [26–28]. One key question is that, in lead halide perovskites, what is the upper limit of the carrier mobility.

As polar semiconductors, carrier mobility is limited by scattering with LO phonons at room temperature. Now that we have obtained the value of $\omega_{LO,eff}$, we can therefore calculate the carrier mobility according to Hellwarth's [25] and Feynman's [29] theories, which have been applied to various semiconductor systems, such as halide perovskites [11, 30], InSb [31], Ca_{1-x}La_xMnO₃ [32], TiO₂ [33], and Bi₁₂SiO₂₀ [34].

The carrier-phonon coupling constants are calculated via $\alpha = \sqrt{m_b e^4 / 2 \hbar^2 \epsilon_*^2 E_{LO}}$, where $1/\epsilon_* = 1/\epsilon_\infty - 1/\epsilon_{static}$, $E_{LO} = \hbar \omega_{LO,eff}$ [35]. Since the effective masses of electrons and holes are different, the coupling constants are different, yielding different mobilities for electrons and holes. The calculated electron-phonon coupling constant $\alpha_{e-ph} = 1.68$ is in excellent agreement with DFT calculated value 1.69 [30]. The small values of $\alpha (< 6)$ suggest that carriers are large (Fröhlich) polarons. Hence the carrier mobility μ follows the expression [25, 29]:

$$\mu = \frac{w^3}{v^3} \frac{3e}{m_b} \frac{\sqrt{\pi} \sinh(\beta/2)}{\omega_{LO,eff} \alpha \beta^{5/2}} \frac{1}{K(a, b)}, \quad (4.5)$$

where e is the elementary charge, m_b is the band effective mass of the electrons or holes, α is the carrier-phonon coupling constant, and $\beta = \hbar \omega_{LO,eff} / k_B T$, with $\hbar$ the reduced Plank constant, k_B is the Boltzmann constant and T is the temperature. The factor $K(a, b)$ is a function of w and v : $K(a, b) \equiv \int_0^\infty du [u^2 + a^2 - b \cos(vu)]^{-3/2} \cos(u)$, where $a^2 = (\beta/2)^2 + R\beta \coth(\beta v/2)$, $b = R\beta \sinh(\beta v/2)$, $R = (v^2 - w^2)/w^2 v$ and the variational parameters w and v are obtained by reaching

the minimum of the Osaka free energy [25, 29].

Calculated mobilities for electrons and holes, and the parameters used for these calculations are listed in Table 4.3. Measured mobilities of 10–100 cm²V⁻¹s⁻¹ on single-crystals [26, 27], agree well with our values, especially the high hole-mobility [28] (~ 210 cm²V⁻¹s⁻¹).

Although the effective LO phonon frequency is same for electrons and holes, the difference in the electron and hole band effective masses results in a difference in the electron–phonon and hole–phonon coupling constants. Since holes have a smaller band effective mass, the constant α_{h-ph} is smaller and therefore hole mobility μ_h is larger according to Eqn. 4.5.

Table 4.3: Calculated 300 K carrier mobility and the parameters used in the mobility calculations in MAPbBr₃. The effective LO phonon mode frequency is obtained by using Eq. (4.4).

ϵ_∞	ϵ_{static}	$\omega_{LO,eff}/2\pi$	Carrier	m_b/m_0	α	w	v	μ (cm ² V ⁻¹ s ⁻¹)
6.7	25	3.46 THz	e	0.25 [36]	1.68	11.4	13.0	83
			h	0.12 [36]	1.17	11.5	12.6	265

From Eq. (4.4) and (4.5), we see that the carrier mobility is dominated/limited by the *lowest-frequency* LO phonon modes, and hence our method gives a good estimation of the *upper limit* of the mobility. In reality, typically, measured carrier mobility shows lower values, due to other scattering channels, such as grain boundaries [37], and ion impurities [38].

4.4 Conclusion

In conclusion, we have studied the THz phonon modes evolution with temperature in the hybrid halide perovskite MAPbBr₃. TO phonon mode splitting is observed near 150 K, which we attribute to the tetragonal–orthorhombic phase transition.

300 K LO-phonon modes in THz range are carefully resolved via direct measurements and extrapolations. The carrier–phonon coupling constants are calculated with the knowledge of the effective LO phonon mode.

We use Feynman's polaron theory to estimate the upper limit of both electron and hole mobility based on scattering with LO phonons, and obtain values that agree well with other measurements.

Our method gives an upper limit to the carrier mobility from a knowledge of the low-frequency phonon modes, without the need to generate carriers via photoexcitation, which can be applied to other polar semiconductors.

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Chapter 5

Role of Carrier Screening and Carrier–Phonon Coupling in Lead Halide Perovskites

In perovskite solar cell research, discussions on phonon modes often involve their limit on carrier mobility via carrier–phonon scattering, but their effect on charge-carrier density, exciton population, interaction with other collective modes and subsequent effect on solar cell performance were not fully studied. Using time-resolved terahertz spectroscopy, we observe a delicate interplay between carriers, phonons and excitons that govern the photo-physical phenomena of the perovskites. Our data show that the combination of phonon emission during carrier relaxation, phonon-assisted exciton dissociation and photo-enhanced carrier screening, ensure a large and long-lived free-carrier population in the system, especially at room temperature. Our results provide fundamental insights into the roles played by carrier–phonon and exciton–phonon interactions towards the excellent photovoltaic properties of hybrid halide perovskites.

5.1 Introduction

The combination of excellent photovoltaic performance and solution processability brought hybrid organometallic halide perovskites into the forefront of solar cell

research [1]. The collusion of favorable properties, such as strong and broadband visible light absorption [2], as well as long ($\sim 1 \mu\text{m}$) and balanced electron and hole diffusion lengths [3, 4], ensure that upon solar illumination, electron-hole pairs can form, dissociate, and quickly drift away from the active regions and towards the electrodes before loss processes such as recombinations occur.

The outstanding photovoltaic performance of perovskite solar cell materials are importantly contributed by phonons, in particular via carrier-phonon scattering. Carrier mobility follow the $T^{-3/2}$ temperature dependence due to scattering off acoustic phonons [5]. Theoretical estimations of carrier mobilities were carried out using polaron theory, i.e. carriers scattering off longitudinal-optical (LO) phonons, from experimentally-obtained phonon mode energies [6–8]. The scattering of LO phonons during carrier recombination leads to linewidth broadening of photoluminescence spectra via the Fröhlich mechanism [9–11]. Phonon relaxation presents a bottleneck that slows down hot-carrier cooling at high excitation densities [12].

Nevertheless, these studies did not directly observe the carriers, phonons and the interaction between them. Time-resolved terahertz (THz) spectroscopy (TRTS), on the other hand, is able to monitor the dynamics of carriers and phonon modes simultaneously. The THz energy range ($1 \text{ THz} = 4.1 \text{ meV}$) overlaps with those of the lowest-lying phonon modes in the perovskites that originates from the vibration of halides and metal ion bonds [13, 14]. The same THz frequency range is also where the carriers interact most efficiently with external electromagnetic radiation, via Drude-type mechanism [15]. This overlap of energies suggests the interesting possibility of detecting carriers, phonons and carrier-phonon interaction in the same THz range. However, there is no substantial observation and discussion of carrier-phonon interactions from TRTS works at the present, and the observed phonon features might be the result of data analysis artifact [16]. Moreover, TRTS enables us to obtain both the real and imaginary parts of the photoinduced change in the complex optical conductivity (or photoconductivity), without the need to invoke Kramers-Kronig transformation. Knowing both the real and imaginary parts

simultaneously restricts the physical models that can explain the data, that is crucial for subsequent data interpretation.

Here, using TRTS, the electron–phonon interaction in the mixed halide-alloyed formamidinium perovskite $[\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3]$ thin film (FCPIB) appears as a change in the phonon mode profile upon photoexcitation. Both bound (i.e. excitons) and unbound (i.e. free carriers) electron-hole pairs are photogenerated. As the free carriers relax towards the band edge, their energies fall below the energies of one or more phonon modes, resulting in a change in the number of phonon scattering (emission and absorption) channels and hence carrier scattering rate. The emitted phonons then participate in phonon-assisted exciton dissociation, resulting in a decrease of phonon spectral weight and concomitant increase of free-carrier density. At the same time, electrostatic screening of the photogenerated electron-hole pairs decreases the exciton binding energy, thus enhancing exciton dissociation (and limits exciton formation) and therefore free-carrier density. This delicate interplay between free carriers, lowest-lying phonon modes and excitons ensures a large and long-lived free-carrier population in the system. We have thus elucidated the critical role played by phonons towards the excellent photo-physical properties of halide perovskite solar cells.

5.2 Sample fabrication

Formamidinium iodide (FAI) was synthesized according to Ref. [17]. The reagents were dissolved in ethanol and recrystallized at $-3\text{ }^{\circ}\text{C}$ overnight. Perovskite precursor solution $[\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3]$ was prepared by dissolving FAI, CsI, PbI_2 and PbBr_2 with respective stoichiometric ratio in DMF/DMSO (4:1 v/v) at $80\text{ }^{\circ}\text{C}$. Z-cut quartz substrates ($10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$) were cleaned thoroughly in Hellmanex IITM solution (1% v/v), deionized water, acetone and isopropanol for 15 min each in an ultrasonic bath. Immediately before deposition of the photovoltaic precursor solution, the substrates were subjected to an air plasma treatment for 5 min and subsequently transferred to a nitrogen glove box. The perovskite solution (1 M)

was spin-coated on z-cut quartz at 1000 rpm for 10 s, and 4000 rpm for 30 s. 250 μL of chlorobenzene were dripped on the sample surface at 15 s of the second step spin-coating. Subsequently, the perovskite layer was annealed at 80 $^{\circ}\text{C}$ for 5 min, 120 $^{\circ}\text{C}$ for 5 min, and 180 $^{\circ}\text{C}$ for 30 min. The thickness of our final polycrystalline FCPB film is (580 ± 20) nm. The sample is mounted in a cryostat with a cryocooler for cooling down to 15 K. The $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$ thin films were prepared by Mr. Hu Hongwei (MSE, NTU).

5.3 Extraction of phonon and carrier contribution

FA-based perovskites have shown more superior thermal stability than MA-based perovskites [18]. Moreover, a thermally and structurally stable FAPbI_3 perovskite can be obtained by the partial substitution of FA with Cs cations [18–20].

Figure 5.1: Frequency-resolved photoconductivity spectra. (a) THz time-domain data of the alloyed FA-perovskite $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$ thin films after optically excitation with 790-nm pump pulses. The photoconductivity is calculated from the transmitted THz electric field through the perovskite film (E_{sam}), z-cut quartz reference (E_{ref}) and the photoinduced change (ΔE). (b) Real part of photoconductivity [$\Delta\sigma_1(\omega)$] (purple circles) obtained by the difference between the photoexcited (navy blue) and the equilibrium THz conductivity (orange). The two peaks show the approximate locations of the lowest-lying TO-phonon modes.

The experimental setup and data analysis methods have been mentioned in Chapter 2. By modulating both the pump and probe beams, both the transmitted THz electric field $E(t_{\text{THz}}, t_{\text{pp}})$ and its photoinduced change $\Delta E(t_{\text{THz}}, t_{\text{pp}})$ are measured simultaneously at different pump-probe time delays t_{pp} (see Fig. 5.1a). At each

pump-probe time delay t_{pp} , we scan the THz emitter delay in reverse, with pump and gate delays fixed. This synchronization procedure ensures that every part of the measured THz pulse experiences the same time delay from the pump pulse [21].

We begin our investigation of FCPIB by measuring the equilibrium complex optical conductivity $\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ at 15 K, as shown in Fig. 5.1b. We observe peaks at 0.85 THz ($\hbar\omega_{TO,1}=3.6$ meV) and 1.80 THz ($\hbar\omega_{TO,2}=7.4$ meV) that originates from transverse-optical (TO) phonon absorption (labeled as mode 1 and 2, respectively). They correspond to a series of TO phonon-modes related to the vibrations of Pb-halide bonds [7, 8]. The conductivity can be described by a Lorentzian profile [15, 22].

THz absorption is strongly sensitive to TO phonons. However, two LO phonon frequencies (ω_{LO}) could be identified from the analysis of loss function, $-\text{Im}[1/\tilde{\epsilon}(\omega)]$ [6, 23, 24].

Figure 5.2: The extrapolated (purple solid) loss function $-\text{Im}[1/\tilde{\epsilon}(\omega)]$, calculated from the fitting parameters of $\tilde{\sigma}(\omega)$ at 15 K, with the loss function directly obtained from the experimental data (black circles).

The loss function displays two Lorentz oscillators allowing us to use the fitting parameters to compute the loss function (Fig. 5.2). We found the longitudinal-optical (LO) phonon modes to be located at slightly higher energies of 1.16 THz ($\hbar\omega_{LO,1}=4.8$ meV) and 3.9 THz ($\hbar\omega_{LO,2}=16.1$ meV), respectively.

Next, we excite FCPIB with 60-fs, $37 \mu\text{Jcm}^{-2}$ laser pulses with a photon energy of 1.57(2) eV. We use temperature-dependent steady-state absorption spectra of FCPIB (Fig. 5.3a) to locate the band gap energy and make sure that the laser

Figure 5.3: (a) Temperature-dependent visible absorption spectra. The red area illustrates the excitation photon energy close to the bandgap energy.. (b) The bandgap energy (1.57 eV) at 293 K is obtained from the linear extension of $(\text{Absorption} \times h\nu)^2$ to the abscissa.

wavelength (780–800 nm) covers the band absorption at all temperatures. By use of Tauc’s analysis [25], the band gap is estimated at 1.57 ± 0.03 eV (Fig. 5.3b). The measurement is measured by Dr. Reinhard Haselsberger (Physics, NTU), using Varian Cary 100 BioTM UV-VIS spectrophotometer in a transmission mode. The photon energy is close to the bandgap energy (Fig. 5.3), which is just enough to create electron-hole plasma, and avoids complex scenarios such as hot-carrier injection or multiple valley excitation.

We then vary the optical path difference to scan the time delay t_{pp} between the optical pump pulses and THz probe pulses, to obtain a full two-dimensional THz spectra of FCPIB photoconductivities (Fig. 5.4a,b).

Our photoconductivities do not display solely a Drude-like characteristic as expected for photogenerated free carriers, but also contain a derivative-like profile located near the two phonon peaks. Such features were also seen in TRTS reports of perovskites, either as a dip in the transmission spectra of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ [26] or an asymmetric photoinduced phonon profile in the photoconductivity spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ [27], that were attributed to the presence of carrier–phonon coupling, though the asymmetry seen here in FCPIB is more pronounced.

The photoconductivity can be quantitatively described by a combination of

Figure 5.4: The (a) real and (b) imaginary part of THz photoconductivity at different pump-probe delays, showing the contributions from Drude-Smith (DS, yellow area) and peak-shift (PS, purple area), and total (dashed black) terms. The DS term arises from photogenerated charge carriers in a disordered background, while the PS term accounts for the change in the oscillator strength and phonon resonant frequency.

Drude-Smith (DS) and peak-shift (PS) contributions:

$$\Delta\tilde{\sigma}(\omega, t_{pp}) = \Delta\tilde{\sigma}_{DS} + \Delta\tilde{\sigma}_{PS},$$

where the DS term is conventionally used to account for free carriers inside a disordered environment [28,29]. We introduce the PS term to account for a change in the phonon profile — in both resonant frequency and oscillator strength — due to photon absorption. A detailed description of this model will be discussed in the next section.

We attribute phonon resonant frequency changes to the combined effects of phonon anharmonicity (predicted by density-functional theory in $\text{CH}_3\text{NH}_3\text{PbI}_3$ [30] and large ionic displacements upon photoexcitation (from ultrafast electron diffrac-

tion data) [31].

5.4 The combined photoconductivity model from phonon and carriers

The THz conductivity in equilibrium due to phonon absorption is usually fitted by a sum of Lorentzian oscillator functions:

$$\tilde{\sigma}_L(\omega) = \sum_{k=1,2} \frac{\epsilon_0 \omega_{pk}^2 \omega}{i(\omega_k^2 - \omega^2) + \omega \gamma_k} - i\epsilon_0 \omega (\epsilon_\infty - 1),$$

where ω_p is the phonon plasma frequency, ω_k is the phonon resonance frequency, γ_k the damping rate, and ϵ_∞ is background dielectric constant. The index k runs up to two to account for two lowest-lying phonon modes in our sample.

If the perturbation to the phonon resonance profile is allowed, the resultant photoinduced change can be written as a first-order differential to the Lorentzian function:

$$\Delta \tilde{\sigma}_L(\omega) = \frac{\partial \tilde{\sigma}_L}{\partial \omega_{pk}^2} \Delta \omega_{pk}^2 + \frac{\partial \tilde{\sigma}_L}{\partial \omega_k} \Delta \omega_k + \frac{\partial \tilde{\sigma}_L}{\partial \gamma_k} \Delta \gamma_k.$$

By carrying out a straight-forward differentiation and assuming that the damping rate is a constant (from phenomenological observation of our data), we can derive the expression for photoconductivity due to the modified phonon resonances:

$$\Delta \tilde{\sigma}_{PS} = \sum_{k=1,2} \left\{ \frac{\epsilon_0 \omega}{i(\omega_k^2 - \omega) + \omega \gamma_k} \Delta \omega_{pk}^2 + \frac{-2i\omega_k \epsilon_0 \omega_{p,k}^2 \omega}{[i(\omega_k^2 - \omega^2) + \omega \gamma_k]^2} \Delta \omega_k \right\} - i\epsilon_0 \omega \Delta \epsilon_\infty.$$

This ‘peak-shift’ model (PS) contains three free parameters: the phonon spectral weight change $\Delta \omega_{p,k}^2$, phonon frequency shift $\Delta \omega_k$, and the change in background dielectric constant $\Delta \epsilon_\infty$. The rest of the parameters were previously obtained from a separate Lorentzian fit to the phonon modes at equilibrium.

This peak-shift model can only account for the phonon contribution, but not for the full photoconductivity observed in FCPIB. We have to consider the contribution

from the free carriers. As in our previous TRTS work on $\text{CH}_3\text{NH}_3\text{PbI}_3$ [27], we employ the Drude-Smith (DS) model to describe the free-carrier signal in a disordered background:

$$\Delta\tilde{\sigma}_{DS} = \frac{\epsilon_0\omega_{pD}^2}{\gamma_D - i\omega} \left(1 + \frac{c_1}{1 - \frac{i\omega}{\gamma_D}}\right).$$

The DS model contains three parameters: Drude plasma frequency $\omega_{pD} = \sqrt{\frac{Ne^2}{\epsilon_0 m^*}}$, where N is the carrier density and m^* the carrier effective mass, Drude scattering rate γ_D which is related to the carrier mobility via the relation $\mu = \frac{e}{m^*\gamma_D}$, and the parameter c (where $0 > c_1 > -1$), accounting for backscattering due to sample disorder.

The final combined model is

$$\Delta\tilde{\sigma}(\omega, t_{pp}) = \Delta\tilde{\sigma}_{PS} + \Delta\tilde{\sigma}_{DS}.$$

From this combined model, we fit the data to extract the photogenerated free-carrier density (via the Drude plasma frequency), carrier scattering rate (via the Drude scattering rate) and the modulation of phonon profiles (via the PS term).

5.5 Carrier–phonon scattering channels: Physical model and experimental data

Before we discuss the fitting parameters, we first introduce the carrier relaxation scheme deduced from our data and shown in Fig. 5.5a,b. This mechanism is an extension of the scheme in GaAs [21]. We will only describe the relaxation from the perspective of electrons, as holes are expected to behave similarly due to their roughly equal effective masses [2, 32, 33].

Immediately after photoexcitation, electrons possess energies (in excess of the bandgap) above the two lowest-lying LO-phonon modes. The energies of the two LO-phonon modes motivate us to partition the electron relaxation process into three

Figure 5.5: (a) An optical excitation generates free electrons that relax from region *i* down towards *iii* delineated by phonon-mode energies $\hbar\omega_{LO,1}$ and $\hbar\omega_{LO,2}$. Only electrons with kinetic energy above the phonon mode energy can both absorb and emit a phonon; only phonon absorption can occur with lower kinetic energy. (b) The number of electron scattering channels reduces from 4 to 3 to 2, as the electrons relax from regions *i* to *ii* to *iii*. (c) Finite-temperature state occupancy calculated from the Fermi-Dirac distribution and density of states in a three-dimensional parabolic band, showing a temperature-dependent high-energy tail. State occupancies are normalized by the total carrier density.

regions *i*, *ii*, *iii*, as shown in Fig. 5.5a. In region *i*, where the electron energy E is larger than that of the two LO-phonon modes ($E > \hbar\omega_{LO,2} > \hbar\omega_{LO,1}$), electrons can interact with the two phonon modes via four scattering channels — phonon absorption and emission from modes 1 and 2.

The electrons then lose energy and enter region *ii*, where $\hbar\omega_{LO,2} > E > \hbar\omega_{LO,1}$. Here, the electrons do not have enough energy to participate in the carrier-phonon scattering process that involves the emission of $\hbar\omega_{LO,2}$ -phonons, so there are now only three energetically-permissible scattering channels left. Similarly, as the electrons relax close to the band minimum in region *iii* ($\hbar\omega_{LO,2} > \hbar\omega_{LO,1} > E$), they cannot emit either $\hbar\omega_{LO,1}$ - and $\hbar\omega_{LO,2}$ -phonons, and we are left with only two scattering channels of phonon absorption. At this point, carrier recombination takes over.

The above picture is strictly valid only at 0 K. At finite temperatures, thermal broadening caused by the high-energy tail in the Fermi-Dirac and hence state occupancy distribution (see Fig. 5.5c), results in the transition between the regions to be gradual rather than step-like. For example, inside region *ii*, even though the

mean energy $\langle E \rangle$ of the electrons obey $\hbar\omega_{LO,2} > \langle E \rangle > \hbar\omega_{LO,1}$, a small fraction of the electrons can still be located in region i , which opens up all four scattering channels there. At room temperature, all four scattering channels open up at all time delays, enabling electron relaxation to take place simultaneously with carrier recombination.

Figure 5.6: (a) Step-like transitions of carrier scattering rate (three horizontal dashed lines), obtained from the Drude-Smith model, in the ratio 3.8:2.9:2. This is close to the 4:3:2 ratio deduced from the number of scattering channels as the electrons relax towards the band edge going from region i to ii to iii . (b) With sufficient thermal energy at 65 K and 285 K, there is a significant fraction of carriers in region i (see Fig. 5.5c), opening up all four scattering channels. This results in the scattering rate at 65 K scaling closer to a factor of 4/2, and a slightly higher value at 285 K.

The experimental evidences of quasi-step-like reduction of scattering channels and our regional assignment of the conduction band are found in the measured Drude scattering rate (Fig. 5.6a,b), which is proportional to the number of scattering channels according to Matthiessen's rule [25]. Figure 5.6a shows that at 15 K, the scattering rates at early (region i : $t_{pp} < 0.6$ ps), intermediate (region ii : 1.2 ps $< t_{pp} < 2.2$ ps) and long (region iii : $t_{pp} > 10$ ps) time delays exist in the approximate ratio 3.8:2.9:2. This is close to the 4:3:2 ratio expected from the number of possible scattering channels in the three regions.

Our interpretation is further supported by data at higher temperatures [65 K $\approx$

5.4 meV, and 285 K $\approx$ 24 meV] — see Fig. 5.6b. Due to thermal broadening at finite temperatures (see Fig. 5.5c), electrons can now populate region i (with four scattering channels) with finite probability. This has two consequences: (1) the 65 K and 285 K scattering rates are similar to that of the 15 K data with four scattering channels, and (2) the change of scattering rate between regions is gradual rather than step-like. The fact that the four-channel scattering rate at 285 K is slightly higher than that at 65 K, which in turn is slightly larger than that at 15 K, is again a consequence of a longer Fermi-Dirac high-energy tail with increasing temperature.

These observations reveal the subtle role phonon energy plays in carrier relaxation. The energies of the lowest-lying phonon modes, relative to the operation temperature of the perovskite solar cells, determines the number of carrier scattering channels and hence the scattering rate, and finally carrier mobility of the photogenerated free carriers.

5.6 The disentanglement of carrier recombination and relaxation

Next we show that the phonons, via their emission by free carriers and/or absorption by excitons, directly affect the density of photogenerated carriers in the material. We do this by monitoring two types of spectral weights: (1) Drude spectral weight, which is proportional to the square of the Drude plasma frequency (ω_{pD}^2), is a direct measure of the number density of photogenerated free carriers $n = \epsilon_0 \omega_{pD}^2 m^* / e^2$, where $m^* = 0.18m_0$ is the electron effective mass [32]; (2) phonon spectral weight, proportional to ω_{pk}^2 , is a measure of the phonon oscillator strength after photoexcitation.

First we have to distinguish between carrier relaxation and recombination in our sample. The former is the process of electrons (holes) cascading down (up) the conduction (valence) band minimum (maximum) that involves a transfer of much smaller energy ($\sim$ meV) with phonons, while the latter is a loss mechanism

Figure 5.7: The linear relationship between $1/n^2$ and pump-probe delay t_{pp} indicates predominantly third-order recombination, especially in the region between 10 ps to 600 ps. The deviation of the data from linearity below 10 ps suggests that carrier recombination is dominant after 10 ps, i.e. in region *iii* near the band edge (see Fig. 5.5a).

of electrons and holes that releases energy of the order of the bandgap. Carrier recombination obeys the rate equation

$$\frac{dn(t_{pp})}{dt_{pp}} = -k_1n - k_2n^2 - k_3n^3, \quad (5.1)$$

where the rate constants k_1 , k_2 and k_3 describe (first-order) trap-state-mediated, (second-order) bimolecular, and (third-order) trimolecular, recombinations, respectively.

Figure 5.7 shows that, at 15 K, $1/n^2$ is linear in t_{pp} from 10 ps to 600 ps, indicating that carrier recombination is predominantly third-order. This is consistent with an Auger recombination mechanism, where an electron-hole recombination is assisted by a third charge carrier. A similar third-order recombination is also seen in $\text{CH}_3\text{NH}_3\text{PbI}_3$ at the same temperature [27]. Figure 5.8a shows how ω_{pD}^2 (and photogenerated carrier density n) changes with pump-probe delay time t_{pp} . The fitting parameters, obtained from the weighted-least-squares linear fit in Fig. 5.7 from 10 – 600 ps, were used to plot the solid line in Fig. 5.8a, and extrapolated down to 0.6 ps and up to 3000 ps. The third-order recombination (solid) curve significantly underestimates the carrier density below 10 ps, which interestingly was

previously marked as the boundary between region *ii* and *iii* in Fig. 5.6a.

Figure 5.8: (a) Time evolution of the photogenerated carrier density n at 15 K. Solid line is the third-order recombination curve plotted using the weighted-least-squares linear-fit parameters (between 10 and 600 ps) in Fig. 5.7, then extrapolated down to 0.4 ps and up to 3000 ps. The curve underestimates the data below 10 ps, implying that additional processes other than recombination occur. The difference between the experimental data and solid curve is indicated by the purple region. (b) Time evolution of the photoinduced change in spectral weight of phonon mode 1 (0.85 THz) and mode 2 (1.80 THz). By comparing (a) and (b), one sees that in region *ii*, a decrease in the spectral weight of both phonon modes is accompanied by an increase in carrier density. This can happen only when phonons are absorbed by the excitons, thereby dissociating the excitons to become free carriers. In region *iii* where the carriers are already near the band edge, phonon emission and absorption slows down, and (third-order) recombination is now dominant.

We now examine the correlation between the carrier and phonon dynamics below 10 ps. To isolate the change in carrier density due solely to phonon absorption/emission, we subtract the raw data in Fig. 5.8a by the third-order-recombination solid line, yielding the purple curve. Figure 5.8b shows the time evolution of the spectral weights of phonon modes 1 and 2. By comparing Fig. 5.8a and 5.8b, we see that in region *ii*, there is an anti-correlation between the carrier and phonon spectral weights — a decrease in phonon spectral weights (of both modes 1 and 2) is accompanied by an increase in the carrier spectral weight. The phonon dynamics in Fig. 5.8b agree with our proposed relaxation scheme in Fig. 5.5a, where no

emission of high-energy $\hbar\omega_{LO,2}$ -phonons is allowed in region *ii* — both $\hbar\omega_{LO,1}$ and $\hbar\omega_{LO,2}$ phonons can be absorbed, but only $\hbar\omega_{LO,1}$ -phonons can be emitted.

In the transition region between *i* and *ii*, as mentioned earlier, the high-energy tail in the finite-energy Fermi-Dirac distribution implies a finite fraction of electrons with energies exceeding $\hbar\omega_{LO,2}$, which after relaxation, results in the emission of the higher-energy $\hbar\omega_{LO,2}$ phonons. Hence in this transition region, we see an increase in the spectral weight of phonon mode 2 as shown in Fig. 5.8b. Similarly, in the transition region between *ii* and *iii*, carriers do not have enough energy to emit the $\hbar\omega_{LO,2}$ -phonons, and there is only a very slow $\hbar\omega_{LO,2}$ -absorption all the way through region *iii* (see long arrow in Fig. 5.8b). A slow emission of $\hbar\omega_{LO,1}$ -phonons (by free carriers) can still take place (due to high-energy tail in the state occupancy in Fig. 5.5c above $\hbar\omega_{LO,1}$), resulting in the formation of excitons.

Figure 5.9: Schematic showing that, without excitons, phonon emission/absorption changes only the carrier energy, not density (red box). For the phonons to change the carrier density, they must be either absorbed by the excitons (causing exciton dissociation and increasing carrier density) or emitted by free carriers (causing exciton formation and decreasing carrier density) (blue box).

The anti-correlation between the carrier and phonon spectral weights can be explained by the phonon-assisted exciton dissociation/formation. In the perovskites, the exciton binding energies of $\sim 10\text{--}16$ meV in FAPbI₃ and MAPbI₃ [34], are in the same range as the LO-phonon mode energies. The excitons dissociate by absorbing an LO-phonon, creating unbound (i.e. free) electrons and holes, resulting in an

increase in carrier spectral weight and hence carrier density. These LO-phonons in turn are provided by the relaxation of the photogenerated carriers as they relax towards the band edge (discussed in the previous section). Since we pump the sample very close to the bandgap, optical excitation should provide just enough energy to create excitons, leading to the coupled dynamics between carriers, phonons and excitons via exciton–phonon coupling that was previously observed in 2D hybrid perovskites via temperature-dependent photoluminescence linewidth broadening [35, 36].

Figure 5.9 shows the coupled dynamics of carriers, excitons and phonons. Without excitons, phonon emission/absorption changes only the carrier energy, not density (red box). For the phonons to change the carrier density, they must be either absorbed by the excitons (causing exciton dissociation and increasing carrier density) or emitted by free carriers (causing exciton formation and decreasing carrier density) (blue box).

Figure 5.10: Time-resolved spectral weight change of (a) free carriers, (b) phonon mode 1 (0.85 THz) and mode 2 (1.80 THz) at 285 K.

We next want to see if the anti-correlation between the carrier and phonon spectra weights, observed at 15 K, is still preserved at room temperature. Figure 5.10a shows the same anti-correlation occurring at 285 K, but now over a much longer timescale — the carrier spectra weight shows a slow but monotonic increase even up to 3 ns, with a concomitant slow and monotonic decrease in the phonon spectral weights (Fig. 5.10b) over the same timescale. It is fascinating that, even

up to 3 ns, the free-carrier density is still increasing and shows no sign of decaying.

5.7 Pump-enhanced free-carrier screening

We now turn to another effect of carrier-phonon coupling on solar cell performance, namely electrostatic screening of electron-hole pairs. The screening cloud surrounding the charge carriers efficiently renormalizes the bare Coulomb potential V_{bare} via the longitudinal dielectric function $\tilde{\epsilon}(\omega, t_{pp})$ [37]. The effective screened potential V_{eff} can be expressed as

$$V_{eff}(\omega, t_{pp}) = \frac{V_{bare}}{\tilde{\epsilon}(\omega, t_{pp})}.$$

Figure 5.11: Electrostatic (or Coulomb) screening factor $\text{Re}(1/\tilde{\epsilon})$ at 0.5 THz as a function of pump-probe delay, at 15 K and 285 K. Note the long-lived screening factor of 0.8 at 285 K even up to 3 ns.

Figure 5.11 shows, at 15 and 285 K, the photoinduced enhancement of free-carrier screening factor $\text{Re}(1/\tilde{\epsilon})$ at 0.5 THz, at different pump-probe time delays, normalized to the value before photoexcitation. At 15 K, though the screening is stronger at short time delays, it quickly recovers towards the equilibrium value, while at 285 K, the screening factor remains at a constant value of 80% (of the equilibrium value) up to 3 ns. The presence of screening reduces the exciton binding energy [38], and thus further enhances exciton dissociation to free electrons and holes. Together with the results of the previous section, at room temperature, both electrostatic screening and exciton dissociation can now compete with carrier recombination,

thus slowing down the decrease of carriers due to recombination and maintaining a large free-carrier population over a long period of time.

5.8 Discussion

Figure 5.12 summarizes the interplay among free carriers, excitons and low-lying phonon modes, based on our present work. Upon photoexcitation with a near-bandgap-energy photon, both free carriers and excitons are generated. The photogenerated free carriers increase electrostatic screening, thus lowering the exciton binding energy and enhances the possibility of exciton dissociation that increases the free carrier density even further. At the same time, the free carriers emit phonons as they relax towards the band edge. These emitted phonons can be subsequently absorbed by an exciton via exciton-phonon interaction, which causes more excitons to dissociate, resulting in even more free carriers and then greater electrostatic screening of carriers, which further facilitates more-efficient exciton dissociation. The positive feedback between pump-enhanced free-carrier screening and phonon-assisted exciton dissociation ensures a large and long-lived reservoir of free carriers in the system. This favorable circumstance is even more pronounced at room temperature — the large thermal energy of the carriers above the LO-phonon mode energies (Fig. 5.10a) ensures more carrier relaxation channels and phonon emission (by carriers). This in turn causes a long-lived ($\sim$ ns) phonon absorption process by excitons (Fig. 5.10b), resulting in enhanced exciton dissociation and therefore large carrier density (Fig. 5.10a).

We were able to come to the above conclusions due only to a combination of technique- and sample-related reasons: (1) we have frequency-resolved (not just frequency-integrated) photoconductivity data, (2) at both low and room temperatures. Also, in the halide perovskites, (3) we can observe the dynamics of carriers and phonon modes in the same THz range, which (4) also lie in the same range as the exciton binding energy (so the excitons can dissociate by absorbing the phonons).

To the solar cell community, our work implies the following requirements for a

Figure 5.12: A schematic showing the interplay among free carriers, excitons and low-lying phonons. Electrostatic screening and phonon-assisted exciton dissociation combine to maintain a large and long-lived free-carrier fraction in the system.

good solar cell material. First, the LO phonon mode energy must be larger than the exciton binding energy, i.e. $\hbar\omega_{LO} > E_B$, so that the excitons can dissociate by absorbing a phonon. Second, the operational temperature T of the device must be such that the thermal energy is larger than the LO phonon mode energy, i.e. $k_B T > \hbar\omega_{LO}$, so that carrier relaxation can result in a large hot-phonon population. Third, it is advantageous that carrier screening be present and long-lived.

5.9 Conclusion

A previous transient absorption work [12] observed a very slow carrier relaxation, and attributed it to the presence of a hot-phonon bottleneck upon photoexcitation. In our present work, due to the ability of TRTS to directly track the carrier density and phonon spectral weights, we found that the hot phonons contribute not only to slower carrier relaxation, but also carrier generation via phonon-assisted exciton dissociation. Our present work goes beyond the usual TRTS methodology of using recombination kinetics to obtain carrier mobility and diffusion length [17, 27, 39, 40]. We present a novel methodology that provides fundamental insights into the coupled dynamics of carriers, phonons, excitons, to see how they cooperate or compete with one another to affect the photo-physical properties, that ultimately determines the

photovoltaic performance of halide perovskite solar cells.

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Chapter 6

Carrier Recombination in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ Thin Films with/without Ligand Treatment

In this chapter, ultrafast carrier dynamics of two $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin-film samples — with / without the ligand treatment — were investigated using TRTS. By modeling the photoinduced change in conductivity with the Drude model, charge carrier density and carrier scattering rate were extracted. Subsequently, carrier lifetime, mobility and diffusion length were obtained. Both samples showed quite outstanding properties as a light absorber: high mobility ($100\text{s cm}^2 \text{V}^{-1} \text{s}^{-1}$) and large diffusion length (exceeding one micron).

6.1 Introduction

Conventional two-step dripping deposition provides an efficient and low-cost method to fabricate large-scale perovskite solar cells (PSCs). However, the dripped PbI_2 layer has a potential to form a dense film, resulting in uncompleted reaction from PbI_2 to perovskite. The unreacted PbI_2 in turn will lead to reduced film stability and solar cell performances [1]. Zhang *et al.* proposed a scheme for an all room-temperature organic ligand-promoted formation for high-quality perovskite films.

Achieving a high PCE of 14.19%, this high-quality perovskite films based PSCs can maintain 95% of their original PCE for as long as 1000 hours in ambient conditions (45%–65% humidity, 20–28 °C) [2]. The room-temperature processing route results in nanostructured reactive intermediates, which significantly reduces the activation energy [3]. This long working lifetime in PSCs thus indicates good stability, due to the successful reduction of unreacted PbI_2 .

It is always important to investigate the physical origin of the high performances of devices. Due to unique advantage of TRTS — extracting carrier concentration and carrier mobility simultaneously [4, 5] — comparative TRTS measurements on this organic ligand treated $\text{MAPbI}_{3-x}\text{Cl}_x$ and the pristine $\text{MAPbI}_{3-x}\text{Cl}_x$ samples are performed.

6.2 Sample processing methods

Z-cut quartz substrates were cleaned and then ultraviolet-ozone treated for 20 min. The perovskite solution were prepared by reacting the $\text{CH}_3\text{NH}_3\text{I}$ (190 mg) with PbI_2 (500 mg) and PbCl_2 (30 mg) in anhydrous N,N-dimethylformamide (1 ml) at room temperature. To deposit perovskite films, the precursor solution was first dripped onto a quartz substrate. This substrate was then spun at 5000 rpm and after six seconds anhydrous chlorobenzene (180 μl) was quickly dripped onto the center of the substrate, and dried on a hot plate at 80 °C for 10 min. Subsequently, the fullerene mixture (8 mg PCBM and 12 mg C_{60} in 1 ml dichlorobenzene) and zirconium(IV) acetylacetonate (ZrAcAc) (2 mg/ml in anhydrous ethanol) were then sequentially deposited by spin coating at 1000 rpm for 60 s and 4000 rpm for 40 s, respectively. Finally, the device was completed with the evaporation of Ag contact electrodes (120 nm) in a high vacuum through a shadow mask. All devices were fabricated in the glove box [6]. The treated sample was treated by organic-ligand vapors at room temperature ca. 10 min. Finally, for both treated and pristine samples, the Ag electrode and fullerene layers were removed by tapes and chlorobenzene wash, respectively.

Samples are grown by Mr. Zhang Hong [Department of Electrical and Electronic Engineering, The University of Hong Kong (HKU)]. The results of this work cannot be published at the present moment, because the methods of sample preparation is now undergoing the patent application process by our collaborator in HKU.

6.3 Experimental conditions

To protect samples from water vapour, after the sample grown on the quartz substrate, a NiO_x thin film was deposited onto the sample [6]. To get rid of possible difference distortion on THz waveforms, a NiO_x thin film was deposited onto the bare substrate as well. We measured static THz spectra on both quartz wafer coated with NiO_x and bare quartz wafer. The obtained transmittance was very close to unity and the frequency-dependent fluctuations in the transmittance were in the range of that in vac-to-vac measurements, showing that NiO_x layer is transparent in the THz range. 1D-TRTS measurements with 400-nm excitation were also done on this quartz wafer coated with NiO_x , and showed no photoinduced change in the THz absorption. Therefore, we can conclude that this NiO_x would not lead to any change in both the static and time-resolved THz spectra.

Since the bandgap of $\text{MAPbI}_{3-x}\text{Cl}_x$ is about 1.6 eV [7], 400-nm (3.1 eV) pump beam was as the above-bandgap excitation beam, generated by letting an 800-nm beam pass through a 0.5-mm thick BBO crystal. With the coated NiO_x layer, we put the sample in vacuum without the worry of possible degradation. In this experiment, we used very small power ($26 \mu\text{Jcm}^{-2}$) in the pump beam and kept the sample at 278 K, because samples were very susceptible to damage by light according to damage threshold of samples from an earlier batch. Low photon density results in small THz absorption, hence the small signal-to-noise ratio in the current batch of samples. The thickness of the pristine sample and the treated sample is 250 ± 20 nm.

6.4 Results and discussions

6.4.1 1D-TRTS results

In time-resolved techniques, the non-zero photoinduced change is observed at a certain pump-probe delay in the delay line, which is defined as $t_{pp} = 0$. In TRTS, the zero pump-probe delay is defined using 1D-TRTS. Figure 6.1 shows, for both pristine and treated samples, a decay process in $-\Delta E/E$, however, the signal to noise ratio is relatively low due to small photoinduced absorption.

Figure 6.1: Frequency-integrated THz spectroscopy. Both pristine and treated samples showed small ($-\Delta E/E < 1\%$) photoinduced THz absorption with a nanoseconds-decay time.

Both samples show a long decay time in $-\Delta E/E$, indicating long carrier lifetimes in both samples. However, due to the limitation of frequency integration, 1D-TRTS represents the decay of the combination of charge carriers and carrier mobility. To further extract carrier density dynamics from $-\Delta E/E$, frequency-resolved TRTS is employed.

6.4.2 2D-TRTS results

The quartz coated with NiO_x layer acts as a reference. The $\text{MAPbI}_{3-x}\text{Cl}_x$ films are deposited on quartz, and subsequently coated with NiO_x layers. As discussed in the last section, all static and photoinduced THz waveform changes are due to the absorption in $\text{MAPbI}_{3-x}\text{Cl}_x$ layers. The extracted photoinduced change in THz

conductivity is $\Delta\tilde{\sigma}_{t_{pp}}(\omega)$, where $\Delta\tilde{\sigma}_{t_{pp}}(\omega) = \tilde{\sigma}_{t_{pp}}(\omega) - \tilde{\sigma}_{-10\text{ ps}}(\omega)$. The complex conductivity $\tilde{\sigma}_{-10\text{ ps}}(\omega)$ at -10 ps is chosen as the response in equilibrium. The real (red circles) and imaginary (blue diamonds) parts of $\Delta\tilde{\sigma}_{t_{pp}}(\omega)$ data are shown in Fig. 6.2 (left for pristine MAPbI_{3-x}Cl_x and right for treated MAPbI_{3-x}Cl_x) with error bars are calculated as the standard error of all data runs, respectively.

Figure 6.2: Photoinduced change in THz conductivity for different delays t_{pp} , after 400 nm excitation. Red circles: the real part of photoconductivity $\Delta\sigma_1(\omega)$. Blue diamonds: the imaginary part of photoconductivity $\Delta\sigma_2(\omega)$. Error bars are calculated from the standard error of all data runs. Solid and dashed lines: real and imaginary fit curves of Drude model.

In general, both samples showed relative quite flat $\Delta\sigma_{1,t_{pp}}(\omega)$ and $\Delta\sigma_{2,t_{pp}}(\omega)$, which can be modeled by Drude model with large carrier momentum scattering rates [4,8,9]: $\Delta\tilde{\sigma}_D(\omega) = \epsilon_0\omega_p^2\tau/(1-i\omega\tau)$, where ϵ_0 is vacuum permittivity, ω_p plasma frequency, τ momentum scattering time. These features in photoconductivity of halide perovskites are quite common, which also are reported on various perovskites,

such as FAPbI₃ [9] and MAPbI₃ [8] thin films. Note that most wiggles are in the range of error bars, indicating they are not true responses from samples, but due to the systematic measurement errors. The best *simultaneous* fits for the complex conductivity are plotted as red and blue solid lines for $\Delta\sigma_{1,t_{pp}}(\omega)$ and $\Delta\sigma_{2,t_{pp}}(\omega)$ for both samples, respectively.

For both pristine and treated samples, from fitting to Drude model, we obtained fitting parameters of (1) $\omega_p(t_{pp})$ and (2) $\tau(t_{pp})$. Subsequently, the carrier density (n) can be calculated via $n(t_{pp}) = \omega_p^2(t_{pp})\epsilon_0 m^*/e^2$, where ϵ_0 is vacuum permittivity and m^* is carrier effective mass. Carrier recombination dynamics of both samples are shown in Fig. 6.3.

Figure 6.3: Carrier concentration dynamics. Carrier densities are calculated from the plasma frequency $\omega_p^2(t_{pp})$ via the relation mentioned in the text. Lines: straight line fits, yielding the slope, dn/dt , as a fitting parameter.

Both samples show they have a long carrier lifetime on a ns time scale. Due to small pump fluences and hence small photoinduced THz absorption, there is a relatively large scattering effect reflected from the data. We estimate dn/dt from the gradient of the carrier density (n) vs. time delay (t_{pp}), by the best least-squares linear fit (red and blue lines above for pristine and treated samples, respectively). We obtain, for pristine MAPbI_{3-x}Cl_x $dn/dt = -3.2 \pm 0.8 \times 10^{12} \text{ cm}^{-3}\text{ps}^{-1}$; and for treated MAPbI_{3-x}Cl_x $dn/dt = -4.3 \pm 1.1 \times 10^{12} \text{ cm}^{-3}\text{ps}^{-1}$.

Mobility and Diffusion Length From scattering time $\tau(t_{pp})$ and $dn(t_{pp})/dt$, carrier mobility (μ) and diffusion length (L_D) can be obtained as a function of

time delay after photoexcitation via the relations $\mu(t_{pp}) = \frac{e\tau(t_{pp})}{m^*}$ and $L_D(t_{pp}) = \sqrt{\frac{2\mu(t_{pp})k_B T/e}{-\frac{1}{n(t_{pp})} \frac{dn(t_{pp})}{dt}}}$. Carrier mobility and diffusion length is shown in Fig. 6.4.

Figure 6.4: Carrier mobility and carrier diffusion length. Both pristine (red circles) and treated (blue squares) samples showed large carrier mobility and long carrier diffusion length.

Figure 6.4 shows that both mobility and diffusion length do not show significant time dependence. To our surprise, both carrier mobility and diffusion length are larger (double) in pristine MAPbI_{3-x}Cl_x. Carrier mobility values are in good agreement with the results measured in MAPbI₃ single crystals (10–100 cm²V⁻¹s⁻¹) [10–14]. Both samples showed micron-scale carrier diffusion length, which is one order magnitude longer than the sample thickness. Therefore, most carriers can transport to the electrodes, which suggests that in MAPbI_{3-x}Cl_x, carrier diffusion length does not play a dominant role anymore, once μm scale diffusion length reached.

6.5 Comparison with time-resolved photoluminescence results

Photoluminescence (PL) measures the radiative recombination events after photoexcitations. PL results shown in Fig. 6.5 are measured by Mr Zhang Hong (EEE, HKU). Figure 6.5a shows that PL intensity of treated MAPbI_{3-x}Cl_x thin films is larger than that of the pristine sample, indicating the radiative recombination rate

Figure 6.5: (a) Static PL spectra and (b) time-resolved PL intensity decay on pristine (black squares) and treated (red circles) samples.

in the treated sample is higher than the pristine one. Moreover, figure 6.5b shows the PL lifetime in the treated sample is longer than the pristine one. By combining the results of Fig. 6.5a and 6.5b, we can conclude that radiative recombination is stronger and long-lived, due to the higher light-emission efficiency in treated samples.

On the other hand, TRTS measurements show that the total recombination rate (radiative and non-radiative) in the treated sample is higher than that in the pristine sample (Fig. 6.3), which agrees with PL results. Note that the lifetime measured in TRTS is of the order of nanoseconds, which is much shorter than the radiative recombination lifetime (hundreds of nanoseconds) (Fig. 6.5b). In solar cell applications, free carrier lifetime limits the power conversion efficiency, together with carrier mobility. This carrier lifetime is the one obtained from TRTS rather than that from time-resolved PL, because PL is not necessarily due to free carrier recombination, but also exciton radiative recombination. In contrast, photoinduced THz absorption is only sensitive to detect free carrier responses via Drude-type mechanism [4].

6.6 Conclusion

Though solar cells fabricated with treated $\text{MAPbI}_{3-x}\text{Cl}_x$ showed higher PCEs than that in pristine $\text{MAPbI}_{3-x}\text{Cl}_x$, we find from TRTS and TRPL measurements that, in

the treated sample, the carrier mobility and diffusion length is smaller, and radiative recombination rate is larger, compared to that in the pristine sample. Our results are surprisingly, and suggest that parameters such as mobility and diffusion length alone do not determine PCEs. Other factors come into play, such as the energy level of the shallow trapped states [15], device architecture (for example laminar versus mesoscopic) [16], etc. Further experimental work need to be carried out, such as time-resolved photoemission electron microscopy (TR-PEEM) [17], photoemission spectroscopy (PES) [18], spectroscopic ellipsometry [19], etc, to study the carrier relaxation and recombination dynamics at interfaces between perovskite layers and the neighbouring electron or hole transporting layers.

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Chapter 7

Stability Study of $\text{CH}_3\text{NH}_3\text{PbI}_3$

One of disadvantages of halide perovskite materials is their poor stability in air with moisture, and even illumination causes degradation. As a non-contact technique, THz-TDS can monitor the low-lying phonon modes in vacuum, in air with moisture or under light illumination. We studied the stability in $\text{CH}_3\text{NH}_3\text{PbI}_3$ with / without LED illumination, in dry air or in vacuum.

7.1 Introduction

In photovoltaic applications, the perovskite layer is located in the centre of a sandwich structure, which is packaged between two stable layers. However, the devices still run the risk of exposure of perovskite to the air, leading to unwanted degradation [1].

Many experiments have been done on perovskite thin films in vacuum, assuming the perovskites are quite stable in vacuum [2–5]. Note that pressure is a very important parameter when we discuss structural stability. For example, the boiling point of water in high vacuum could be as low as ~ 220 K, while under atmospheric pressure it is ~ 373 K; superconducting $(\text{H}_2\text{S})_2\text{H}_2$ exists not only at low temperature but also under high pressure [6]. Although the structural phase transition temperatures obtained from thin-film samples under vacuum are consistent with those measured on single crystals under atmospheric pressure, the study on possible morphology

changes on thin films has not attracted much attention. Much work has been done on the effect of irradiation, heat and moisture on sample degradation.

In the THz range, low-lying phonon modes are observed and suggested to strongly couple with free carriers [7, 8]. Therefore, studies on perovskites under the AM 1.5 illumination and under vacuum have application and fundamental interests. To investigate this property, we employed THz-TDS to monitor the change in the phonon modes by light-emitting diode (LED) illumination as a function of illuminating time. Through monitoring the phonon responses — both resonant frequency and oscillator strength, LED-illuminated THz-TDS measurement can shed light on whether irradiation of LED light causes degradation, under constant sample temperature and vacuum conditions.

In this chapter, a series of THz-TDS measurements have been made on samples grown by the same method (one-step spin coating), under different vacuum and illumination conditions. Table 7.1 lists the samples under different conditions.

Table 7.1: THz-TDS measurements on three $\text{CH}_3\text{NH}_3\text{PbI}_3$ samples under different conditions. All samples measured in this chapter are grown by the same method: one-step spin coating.

Sample	LED illumination	THz-TDS experimental conditions
S3	✓	Dry air ($\sim 2\%$ relative humidity)
S4	✓	Vacuum (10^{-6} mbar)
S9		Vacuum (10^{-6} mbar)

7.2 Stability under LED illumination

7.2.1 Sample processing method

Z-cut quartz substrates ($10 \times 10 \times 1$ mm) were cleaned thoroughly in Hellmanex[®]II solution (1%v/v), deionized water, acetone and isopropanol for 15 minutes each in an ultrasonic bath. Immediately before deposition of the photovoltaic precursor solution, the substrates were subjected to an air plasma treatment for 5 minutes and subsequently transferred to a nitrogen glove box. The $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2

components were dissolved in stoichiometric ratio to form the precursor solution (30 wt% in dimethylformamide) for spin coating, followed by heating on a hotplate at 100 °C.

All $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) samples examined in this chapter were grown by Dr. Teddy Salim (MSE, NTU).

7.2.2 Experimental setup

To simulate the standard solar simulation source to illuminate the perovskite, a home-made LED array was used. LEDs were bought from RS Components. Since both the light from LEDs and the THz beam are propagating towards the sample, the LED array was made as a ring-shape array, which allows THz beam to propagate through the aperture at the centre of the LED array. The detail of this home-made LED array is shown in Fig. 7.1 — the LEDs are connected in parallel and soldered between two circular shape wires. This design enables the rest of the LEDs to light up, even in the event that one or more LEDs are broken.

Figure 7.1: Home-made LED array for LED illuminated THz-TDS experiment. (a) LED off and (b) LED on.

The prerequisite is to identify how this light source compares with simulated AM 1.5 source. Since the spectra of the home-made LED array are different from the standard solar spectra, and the absorbed photon to charge-carrier yield is a function of photon energy, light intensity is not a suitable parameter for calibrating our LED

light source. Short-circuit current is often used as an indicator of the photovoltaic performance of a solar cell [9]. In turn, for a specified solar cell, short-circuit current can be an indicator of the light source irradiation. Therefore, the relative short-circuit photocurrent is employed rather than the relative light intensity.

Figure 7.2: (a) Side and (b) top view of short-circuit photocurrent measurement using a silicon solar cell illuminated by the home-made LED array.

Figure 7.3: A top view photograph of the LED array assembled on the sample holder taken (a) with and (b) without a flash. Both apertures of the LED array and the sample holder are coaxial, to ensure the THz beam passing through.

We employed a commercial silicon solar cell to calibrate the standard photocurrent J_0 under a standard AM 1.5 light source (23.0 mA, measured by Mr. Hu Hongwei, MSE, NTU). With his help, I measured the photocurrent in the silicon solar cell, under the illumination from the home-made LED array. With 1-cm distance between the LED array and the silicon solar cell (Fig. 7.2a), the measured

current is 5.75 mA, which is $\sim 25\%$ J_0 . The setup of this photocurrent measurement is shown in Fig. 7.2.

7.3 Results and discussions

7.3.1 THz-TDS measurements with LED illumination

With the setup of the sample holder with the assembled LED array (Fig. 7.3), room-temperature LED-illuminated THz-TDS studies have been done in dry air and in vacuum.

Here, we show THz spectra, XRD results and SEM topological image of sample S3 in dry air and sample S4 in vacuum in Fig. 7.4. After a few-hours (few-days) exposure to dry air (vacuum) under LED illumination, the round region has been bleached to a lighter color sample S3 light yellowish; sample S4 transparent, while of this region, the sample still original brown color (see insets of Fig. 7.4c and Fig. 7.4d). Changes in color indicate the samples have either degraded or become much thinner. The thickness change in sample S3 is from ~ 230 nm to 170–190 nm; in sample S4 is from ~ 230 nm to 20–40 nm. The real part of THz conductivity is shown in Fig. 7.4a for sample S3 and Fig. 7.4b for sample S4, representing how absorbance in THz range have changed.

We can see that in sample S3, the two original peaks (at 1 and 1.9 THz) have merged into one asymmetric peak at 1.6 THz. From the literature, we know that the two original peaks originate from the vibration modes of Pb–I bonds, which is the fingerprint of the perovskite structure. In the first two hours, in sample S3, both the peak frequency and peak amplitude of σ_1 remain the same as before illumination. After 6 hours, the two peaks in σ_1 disappeared, and a new phonon mode appears at 1.6 THz. This observation suggests the sample has degraded after 6-hour LED illumination in dry air. The sample was surrounded by air with RH 2%, so the water still can react with the sample, slowly though. Most probably the degraded part of the sample S3 is PbI_2 (pure PbI_2 gives a yellow color). We therefore proceeded to

Figure 7.4: (a) and (b) THz spectra, (c) and (d) SEM images on (left) sample S3 and (right) sample S4 after the measurements. (f) XRD results on bare quartz, sample S3 and sample S4. Insets in (c) and (d) are photos of samples S3 and S4 after THz-TDS measurements.

measure a pure PbI_2 thin-film sample.

Figure 7.5 shows the real part of conductivity σ_1 of PbI_2 thin-film samples, displaying a peak at 1.6 THz, which agrees well with inelastic neutron scattering results [10]. This supports our speculation that the 1.6 THz peak arises from the absorption of PbI_2 . However the asymmetric peak suggests the presence of other chemical components. The XRD pattern of sample S3 (in dry air, shown in Fig. 7.4f)

Figure 7.5: The real part of THz conductivity of PbI_2 at 300 K.

supports this — the strong peak at 12.6° is from PbI_2 (also observed in Ref. [1] on degraded MAPbI_3 thin films), while the peak at 16.4° is of unknown origin. In general, the film still maintains its original morphology (interconnected network of perovskite crystals) from SEM pictures. However, at high magnification, we can see holes forming on the surface of the crystals, and the crystals also appear to crack.

In contrast, THz spectra on sample S4 show that only the amplitude of the phonon modes changed with time, not the peak frequencies. These features suggest that the sample in vacuum was not degraded, and the slightly smaller absorbance from the phonon modes is more likely due to the peeling off the crystal by the vacuum, which is supported by the significant drop in the sample thickness from ~ 230 nm to 20–40 nm. The XRD peak at 14° is from the perovskite structure, which confirms that the remaining film are still perovskites. Since the perovskite layer has become much thinner, the crystals become much sparser, from the SEM image (Fig. 7.4d).

Our work above shows that LED-illuminated samples will either degrade by reacting with water in the air or be peeled off by vacuum. Since the sample degradation should be strictly avoided during the study for investigating the physical properties of perovskites, the sample must always be kept away from the moisture.

Note that both LED illumination and vacuum can lead to the sample instability, therefore, perovskite stability study without LED illumination is required, which is

what we present below.

7.3.2 THz-TDS measurements without LED illumination

Now we turn off the LEDs and keep the samples at 285 K in vacuum. Note that THz radiation causes only negligible degradation, since the energy of THz photon is of the order of meV ($1 \text{ THz} = 4.1 \text{ meV}$), which is smaller than the thermal energy at 285 K ($285 \text{ K} = 24.6 \text{ meV}$).

Figure 7.6: THz conductivity of samples (a) S9 and (b) S4 as a function of time in vacuum. For sample S4, this time in vacuum is same as LED illumination time.

We plot evolution of $\sigma_1(\omega)$ on samples S9 (LED off) in Fig. 7.6a and S4 (LED on) in Fig. 7.6b (same as Fig. 7.4b) together for comparison. THz spectra obtained from both samples S9 and S4 showed a drop in THz absorption. Interestingly, without LED illumination, the vacuum was still able to decrease the THz absorption of sample S9. However, in sample S9, the decrease in the amplitude of the phonon peaks stopped after 96 h, which suggests vacuum can only peel off the surface, not the interior, of the film.

7.4 Conclusion

MAPbI₃ perovskite thin film is not stable under LED illumination. Even ambient as low as 2% RH dry air can degrade the sample: (1) the 1.6-THz phonon mode is observed in both degraded sample S3 and pure PbI₂ thin film; (2) XRD results of degraded sample S3 agree with the literature that the 12.6° peak is from PbI₂.

Although sample S4 shows significant drop of the amplitude of two peaks in THz spectra, the 14° peak in XRD confirms sample S4 is still perovskite after more than 100 hours of LED illumination in vacuum. The large decrease in the thickness of sample S4 suggests the perovskite has been peeled off significantly.

Without LED illumination in vacuum, sample S9 still shows a similar decrease in THz-phonon-mode absorption in the early 10s hours and becomes stable after 96 hours. Therefore both vacuum and LED illumination can cause perovskite films to be peeled off, while LED illumination hastens this process.

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Chapter 8

Conclusions

Based on the work that has been done in this thesis, we are now able to answer the following questions regarding the lead halide perovskites.

How do low-frequency phonon modes evolve with temperature, especially approaching the structural phase transition temperatures? The low-lying optical phonon modes are related to the Pb–X (X = I, Br or Cl) vibrations — either the buckling of the X–Pb–X angles, or the stretching of the Pb–X bond. The orientation of the C–N axis of cation CH_3NH_3 is fixed only in the orthorhombic phase and not in the tetragonal and cubic phases. Thus, approaching the orthorhombic–tetragonal phase transition temperature, the unit-cell volume, hence the Pb–X bonds, will change.

These changes can be observed as phonon mode splitting around the orthorhombic–tetragonal phase transition temperature, by measuring the THz spectra at different temperatures.

How do these phonon mode properties affect the photovoltaic performances? Phonon modes yield information on the crystal structure, which generally will indirectly affect the transport properties of semiconductors. According to Fröhlich’s polaron theory, in polar semiconductors, a free electron will produce a local displacement via attracting the positive ions and repelling the negative ones.

In this circumstance, carrier mobility is often limited by the scattering between carriers and the lowest-frequency LO phonon modes, which can be calculated by Feynman’s polaron theory.

How do photo-generated free charge carriers and these low-lying optical phonons couple with each other, upon the photoexcitation on a ps–ns timescale? In semiconductors, free carriers are generated through the interband transition from the valence band to the conduction band. The conventional picture is that, subsequently, carriers will either gradually relax to the band minimum or recombine.

Meanwhile, THz spectroscopy shows that both free carriers and low-lying optical phonon modes interact with electromagnetic radiation in the THz range. There have been reports of carrier–phonon coupling in lead halide perovskites. However, these reports were not able to probe the dynamics of the photogenerated carriers and phonon modes simultaneously, which our 2D-TRTS technique could.

Through near-bandedge excitation, we employed time-resolved THz spectroscopy to study the FA-based alloyed perovskite thin films. We found, at 15 K, in the first 10 ps, strong signatures of the interplay between carrier relaxation and optical phonon populations, on top of a third-order recombination background. We see correlations between carrier recombination rate and the number of carrier scattering channels, as we vary the pump-probe time delay and lattice temperature. This is further confirmed by dynamics of the THz phonon populations. Carrier density enhancement at 2 ps after the excitation indicates that phonon-assisted-exciton dissociation and formation happened in the first 10 ps. At 285 K, this process even shows up to 3 ns due to efficient phonon-assisted exciton dissociation. At the same time, electrostatic screening of the photogenerated electron–hole pairs decreases the exciton binding energy, thus enhancing exciton dissociation (and limits exciton formation) and therefore free-carrier density. This delicate interplay between free carriers, lowest-lying phonon modes and excitons ensures a large and long-lived free-carrier population in the system. All these are accompanied by a phonon blue-shift,

which is attributed to the phonon anharmonicity and the large ionic displacements upon the excitation.

The longer the diffusion length, the higher the photovoltaic efficiency?

High carrier mobility and long balanced electron–hole diffusion lengths are keys of the success of perovskite solar cells. Researchers have been using novel treatment methods, compositional engineering or designs for the photovoltaic devices to further improve efficiency, stability and reliability.

Recently, organic ligand treatments are frequently employed to enhance the reaction of PbI_2 during sample fabrication, and indeed the efficiency is higher. It is interesting to know this improvement is due to the enhanced carrier mobility and carrier diffusion length. We performed time-resolved THz spectroscopy on both pristine and organic-ligand treated samples under identical experimental conditions. Our results reveal that while both samples showed high mobility ($100\text{s cm}^2\text{V}^{-1}\text{s}^{-1}$) and long diffusion length (several microns), surprisingly, the pristine sample possesses even higher carrier mobility and longer diffusion length than the treated one. This result suggests that, beyond a certain large value of carrier mobility and diffusion length, there is no longer a positive correlation between carrier mobility and PCE. Other factors must come into play, such as better morphology or better interface contact with electron / hole transporting layers.

Are the halide perovskites stable under various conditions, such as moisture, light illumination and/or low pressure (vacuum)? For one-step method grown MAPbI_3 , under LED illumination, even 2% relative humidity leads to the perovskite degradation — two THz phonon modes merges into one at 1.6 THz after 6-hour exposure. This 1.6 THz mode belongs to that of PbI_2 , which is further confirmed by XRD data.

In vacuum (10^{-6}mbar) and under LED illumination, no degradation was observed in MAPbI_3 film: both THz spectra and XRD results show that the film is still the original perovskite, though with a smaller thickness. Even without LED

illumination, THz-phonon-mode absorption decreases during the first 96 hours, and then stays constant after that. Therefore both vacuum and LED illumination can cause perovskite films to be peeled off, while LED illumination hastens this process.

Chapter 9

Future Work

We suggest further studies to elucidate the carrier and phonon dynamics in halide perovskites, via not only the optical excitation to generate carriers, but also a large population of excited-state phonons. To achieve the latter, a high-power THz pulse generation setup is needed to excite low-frequency phonon modes. Combined with TRTS and transient absorption spectroscopy, intense THz pump will help to further unveil the key role of low-lying phonon modes in perovskite solar cells.

9.1 LiNbO₃-based intense THz electromagnetic radiation generation

High-power THz pulse generation has been intensively used in the study of unexplored nonlinear phenomena, involving nonlinear optical and transport processes [1–4]. To observe these nonlinear dynamics, intense-THz-pulse generation is necessary. Due to its large electro-optic coefficient ($d_{33} = 27$ pm/V) and its high optical transparency over a broad spectral range (350–5200 nm), LiNbO₃ crystals have the ability to yield high-power THz pulses via optical rectification (discussed in Chapter 2) when fs pulses pass through the crystal [5].

THz generation via optical rectification requires both the group velocity of the optical pulse n_{opt}^g and phase velocity of the THz pulse n_{THz} to be the same in a

MgO:LiNbO₃ crystal, $v_{opt}^g \cos \theta = v_{THz}$. However, in a LiNbO₃ crystal, $n_{opt}^g = 2.3$ at 780 nm and $n_{THz} = 5.2$ [6], which implies that a large-angle tilted front is needed.

Figure 9.1: (a) Schematic of the THz pulse generation setup for the tilted-pump-pulse-front scheme. The 4f-lens configuration consists of two cylindrical lenses L1 and L2 with respective focal lengths of f_1 and f_2 in horizontal direction. (b) Schematic of the high-electric-field setup. The off-axis parabolic mirrors PM1, PM2, and PM3 have different focal lengths and diameters. Taken from Ref. [7]

A phase-matched THz pulse generation requires a tilted-pump-pulse-front scheme, as shown in Fig. 9.1a. A grating is used to generate a tilted-pulse front, and a pair of cylindrical convex lenses (L1 and L2) are used in a four-lens geometry, to ensure a good spatial overlap among all frequency components. The optical beam is normally incident to the LiNbO₃ crystal, while the tilted pulse front is parallel with the output LiNbO₃ surfaces. According to Ref. [7], the output THz beam can be regarded as a collimated rather than a point source.

We can use one reflected parabolic mirror to focus the THz beam (PM1 in Fig. 9.1b). Moreover, for a certain intense THz source, the maximum electric field amplitude is scaled by the beam size ($\pi d^2/4$). According to the Abbe diffraction limit, the beam diameter d and the focal length L have the relation $d = \lambda/2NA$, for a certain wavelength λ , where NA is numerical aperture. Parameter NA is equal to $n \sin \theta$, where n is the refractive index of the lens medium, and $\sin \theta = d/(d^2 + L^2)$. To obtain a minimum beam size, two additional parabolic mirrors are needed to get a maximum in $\sin \theta$, since $n = 1$ for reflected parabolic mirrors in air. As shown in Fig. 9.1b, a parabolic mirror system with a large ratio of d/L is needed. Therefore, we need to use two more parabolic mirrors PM2 and PM3 in Fig. 9.1b — PM2 is

for increasing the aperture of THz beam, and PM3 is the one whose ratio of d/L is the smallest in the system.

We aim to obtain a peak electric field of several MV/cm at the sample position (see Fig. 9.1b) as a THz pump in further studies.

9.2 Optical-pump intense-THz-pump THz-probe spectroscopy on halide perovskites

Once the intense THz setup is built, in the proposed research, we will address a crucial open question in perovskite solar cell community: how does the carrier-phonon coupling affect carrier scattering rate and carrier population via carrier-phonon-exciton coupling.

In particular, we will detect and explore the phenomena of carrier-phonon coupling in a mixed-cation perovskite $[\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3]$, using optical-pump intense-THz-pump THz-probe spectroscopy (OPTPTP), which is based on our preliminary TRTS results (Chapter 5). We will probe the carrier and phonon dynamics after photogenerated carriers (via optical excitation), THEN excite THz optical phonon modes (via intense THz excitation), to investigate the THz optical phonon lifetime, anharmonicity, carrier scattering rate and carrier population dynamics in a sub-picosecond-to-nanosecond (sub-ps-to-ns) time scale.

Previous studies concerned (1) the lowest-lying longitudinal-optical (LO) phonon modes (whose frequency is in THz range) limiting the carrier mobility via Fröhlich’s mechanism, (2) significant carrier-phonon coupling signature and (3) hot phonon bottleneck limiting hot carrier cooling. Furthermore, a very recent outlook put forward by Jacques-E. Moser [8], in his latest News & Views “Slow recombination unveiled”, that further studies using time-resolved THz spectroscopy are needed to “unravel the fast processes that occur during the thermalization of photocarriers”, as well as to identify “the origin of low-frequency vibrations that are seemingly at the heart of the unique properties of lead halide perovskites”. Till now, all

studies are either only probing the carrier cooling, or to measure carrier mobility, diffusion length and recombination rates, while the possible key role played by the low-frequency phonon modes have not been fully investigated experimentally. This OPTPTP can be a powerful technique to push the entire solar cell community to look for new solar cell materials not only from those “direct bandgap semiconductors” and “proper energy scale of the bandgap” point of view, but also from a low-frequency phonon modes point of view. This, we hope, will usher a new and fruitful direction in perovskite research.

The aims of this study are: (1) to observe the responses of photoinduced carriers and phonon modes under the influence of intense THz fields; (2) to disentangle the contributions to carrier scattering rate, carrier population, phonon mode oscillator strength and phonon peak shift upon the optical and intense-THz excitations; (3) to elucidate mechanisms of photogenerated carrier relaxation, carrier recombination, and phonon-assisted exciton dissociation/formation; and (4) to characterize the low-frequency phonon decay time scale and carrier–phonon coupling strength upon intense THz excitation.

9.3 Optical-pump intense-THz-pump white-light-probe spectroscopy

Transient absorption (TA) spectroscopy is a powerful technique to probe carrier relaxation processes from the perspective of interband transition. A hot-phonon bottleneck effect has been observed in previous TA studies [9, 10]. Most probably, these hot phonons are the low-frequency THz phonons. Instead of excitation density dependence, intense THz pump may be able to “heat up” the phonon modes even with weak pump excitations.

Based on the TA system, intense-THz-pump will induce a long-lived large phonon population, hence can further slow down the carrier energy relaxation and carrier recombination. Together with OPTPTP, we aim to fully elucidate the behavior of

photogenerated carriers.

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