Carrier and exciton dynamics in halide perovskites

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Carrier and exciton dynamics in halide perovskites

Qing CHANG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

Oct 2020

Carrier and exciton dynamics in halide perovskites

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Supervisor: Associate Professor Elbert CHIA

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

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

Oct 2020

Statement of Originality

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

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Abstract

Ever since the first perovskite-based solar cell (PSC) was reported in 2009, reported power conversion efficiencies (PCEs) of PSCs showed a rapid increase from 3.8% to now 25.5%. The reasons for the high PCEs include the large absorption coefficients, high carrier mobilities, and long balanced electron-hole diffusion lengths. Free carriers dominate at low excitation densities, while excitons at high excitation densities. The latter condition is widely used in light-emitting diodes and lasers. To determine the photovoltaic performance of PSCs, the charge carrier transport properties of the perovskites should be characterized. In transient absorption (TA) spectroscopy, free carriers and excitons both contribute to the transient signals, while time-resolved THz spectroscopy (TRTS) is sensitive to both carriers and phonon modes in lead halide perovskites. Hence, these ultrafast techniques are useful tools to characterize charge transport properties of lead halide perovskites. My thesis includes studies that use TA to disentangle the time-resolved free carrier and exciton contributions in mixed-cation lead mixed-halide perovskites, and also use TRTS to disentangle carrier and phonon dynamics in all-inorganic perovskites. Knowing the physics behind these materials after photoexcitation could give useful information to device scientists and sample growers.

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Chapter 1

Introduction

In this chapter, I will introduce the motivation of my thesis. Detailed information of each chapter are mentioned.

1.1 Motivation

Ever since the first perovskite-based solar cells (PSCs) were reported in 2009, their reported power conversion efficiencies (PCEs) showed a rapid increase from 3.8% to now 25.5% [1,2]. The reasons for the high PCEs include the large absorption coefficients [3,4], high carrier mobilities [5], and long balanced electron-hole diffusion lengths [6]. Free carriers dominate at low excitation densities, while excitons at high excitation densities [7]. The latter condition is widely used in light-emitting diodes and lasers [8,9]. To determine the photovoltaic performance of PSCs, charge carrier transport properties of the perovskites should be characterized. In transient absorption (TA) spectroscopy, free carriers and excitons both contribute to the transient signals [10,11], while time-resolved THz spectroscopy (TRTS) are sensitive to both carriers and phonon modes in lead halide perovskites [12]. It is therefore essential to disentangle the charge carrier dynamics from the exciton or phonon mode dynamics in these cases.

Thanks to the availability short femtosecond (fs) laser pulses, ultrafast techniques

such as TRTS and TA have been developed [13,14]. TRTS probes ultrafast change in milli-electron-volt energy (meV) scales, and so can unravel charge carrier dynamics after photoexcitation [13, 15]. TA probes ultrafast change in electron-volt (eV) energy scales, and can disentangle carrier and exciton dynamics after photoexcitation [10,11]. Hence, these ultrafast techniques are useful tools to characterize charge transport properties of lead halide perovskites. Elucidating the carrier, exciton, and phonon mode dynamics is my main work in this thesis.

1.2 Outline of the thesis

This thesis focus on the extraction of carrier dynamics in various lead halide perovskites using ultrafast techniques. The thesis is organized as follows:

- Chapter 2. Introduction to techniques used in my work: Terahertz time-domain spectroscopy (THz-TDS), TRTS, and TA. Basic principles of THz generation and detection, common models including the Lorentz model, the Drude-Smith model, and the plasmon model, as well as data analysis procedures in THz-TDS, TRTS, and TA are described.
- Chapter 3. Brief review of lead halide perovskites. The unique physical properties, including large optical coefficients in visible light range and shallow defect levels, arising from band structure of lead halide perovskites. Related studies on carriers, excitons, and phonon modes in perovskites after photoexcitation are surveyed.
- Chapter 4. Related studies on overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ and stoichiometric all-inorganic CsPbI_2Br are introduced. Our TRTS results on both overstoichiometric and stoichiometric all-inorganic CsPbI_2Br are described.
- Chapter 5. Related studies on mixed-cation lead mixed-halide perovskite thin films are introduced. Our TA measurements and analysis on the mixed-cation lead mixed-halide $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$ thin films are presented.
- Chapter 6. A combination of THz-TDS and X-ray diffraction (XRD) was used to recognize CsPbBr_3 , CsPb_2Br_5 , and Cs_4PbBr_6 in multi-phase samples. THz-TDS

and XRD results on the Cs-Pb-Br mixture systems are presented. TRTS results on the dual-phase $\text{CsPbBr}_3\text{--CsPb}_2\text{Br}_5$ are presented.

- Chapter 7. Main results of this thesis are summarized.
- Chapter 8. Future work.

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Chapter 2

Experimental Techniques and Data Analysis Methods

In this chapter, ultrafast techniques and relevant data analysis procedures used in this thesis are described. The chapter contains two parts: (1) THz-TDS and TRTS; (2) TA.

Thanks to the invention of high fluence fs-pulse laser, researchers can perform pump-probe measurements to detect ultrafast dynamics in sample systems. Ultrafast pump-probe techniques like TRTS and TA are used to study the dynamics of carriers, excitons, phonons in materials. The difference in the probe energy ranges of TRTS and TA leads to different results that support and complement each other.

2.1 THz-TDS and TRTS

THz frequency lies between microwave and infrared regions of the electromagnetic spectrum, whose energy can be expressed in units of meV or cm^{-1} , with $1 \text{ THz} \approx 4.1 \text{ meV} \approx 33.3 \text{ cm}^{-1}$. THz techniques are ideal candidates to probe free carriers, collective modes, and electronic transitions at low energy [1].

2.1.1 THz-TDS setup — THz generation and detection

There are two commonly used methods to generate terahertz radiation using fs laser pulses: one is using photoconductive (PC) antennas and the other one is using optical rectification in nonlinear crystals.

THz generation based on photoconductive antennas As shown in Fig. 2.1a, a biased PC antenna can generate a THz pulse after being excited by a fs laser pulse with photon energy above the bandgap of the antenna material. Conventional antennas (see Fig. 2.1) used for THz generation consists of two metal electrodes on a semiconductor substrate. A laser beam shining onto the gap between the electrodes injects photocarriers, and an applied static bias field then accelerates the carriers. As a result, the time-varying photocurrent generates THz pulses.

Figure 2.1: THz generation (a) and detection (b) based on a photoconductive antenna. Taken from Ref. [2]

THz generation based on nonlinear crystals Compared to THz generation based on PC antennas, in the case of THz generation in nonlinear crystals, incident laser pulses undergo nonlinear frequency conversion, e.g., difference frequency generation [3,4]. THz generation from non-centrosymmetric crystals after far-infrared pulse excitation was first demonstrated by Yajima *et al.* [5]. For a laser pulse with

Gaussian shape with the expression as $E(t) \sim E_0 e^{-at^2} e^{i\omega t}$, the optical injection-induced polarization $P(t)$ has a time-varying expression

$$|P(t)| \propto E_0^2 e^{-2at^2}. \quad (2.1)$$

Therefore, incident intense fs pulses can generate THz pulses with the envelope of the fs pulses as shown in Fig. 2.2. A good phase matching condition enhances the conversion efficiency, hence, the fine-tuning of nonlinear crystal angle is required.

Figure 2.2: Schematic of THz generation in a nonlinear crystal. The Gaussian shape pulse (dotted line) propagating through the nonlinear crystal (NL) generates THz radiation (dashed line). Taken from Ref. [6]

THz radiation obtained via focusing a laser beam in the air is a method to realize wideband THz pulses with a high-field of ~ 8 MV/cm covering 0.1–10 THz [7]. A potential method to generate wideband THz pulses is realized via spintronic devices [8], for which the generated THz pulses cover a wide spectral range up to ~ 12 THz without the absorption of phonons [8].

Due to the weak energy per THz pulse, the power measurement of a THz beam is often based on thermal absorption. The pyroelectric infrared detector used in THz power measurement has responsivity reaching 400 kV/W [9]. There are two commonly used methods to obtain THz spectra based on: (1) Photoconductive antennas and (2) electro-optic crystals.

THz detection based on photoconductive antennas PC antennas can be used to detect THz pulses in the time domain. As shown in Fig. 2.1b, the THz field serves as a bias field to accelerate the photogenerated carriers that were created by the fs pulses. The transient photocurrent is proportional to the applied THz field amplitude. By measuring the photocurrent at different time delays t_{THz} , the THz probe in the time domain can be mapped out.

Figure 2.3: THz detection based on nonlinear crystals. The symbol $\lambda/4$ denotes a quarter-wave plate. Taken from Ref. [6]

THz detection based on nonlinear crystals The detection of THz pulses using nonlinear crystals is based on the Pockel effect as known as the electro-optic (EO) effect, which is an inverse effect of optical rectification. Figure 2.3 shows how THz signals are obtained. When a THz pulse hits the electro-optic crystal, it induces birefringence (i.e. a change in polarization) in the crystal. A weak optical fs pulse passing through the EO crystal is modulated by this birefringence with change in its polarization. Because the fs pulse is much shorter than the THz pulse, the induced change in polarization is proportional to the instantaneous THz field. After passing through a Wollaston prism (WP), the optical pulse splits into pulses with polarizations along x and y directions. The balanced photodiodes (BPDs) can then recognize the difference between the intensities of the two beams with x and y polarizations. Without the THz pulses to modulate the detecting EO crystal, the

difference in the measured BPD intensities is zero. In the presence of THz pulses to cause birefringence in the EO crystal, the difference ΔI is proportional to the instantaneous value of the THz field.

THz-TDS setup THz-TDS is based on coherent detection on both amplitude and phase of the THz field passing through sample systems. Here I will introduce two setups used in my experiments: (1) commercial THz-TDS (Teraview, TPS Spectra 3000) spectrometer and (2) home-built THz-TDS spectrometer based on 1 kHz Coherent Legend-Elite laser.

Figure 2.4: (a) Photograph and (b) working diagram of a commercial TPS Spectra 3000. Taken from Ref. [10]

THz generation and detection in the TPS Spectra 3000 are based on PC antennas. As shown in Fig. 2.4, the fs laser beam (800-nm center wavelength, Coherent Vitesse) is divided into a THz generation beam and a gating beam. The time delay t_{THz} between the two beams is adjusted by a delay stage. In our home-built THz-TDS setup, THz generation and detection are both realized with a 1-mm thick ZnTe crystal.

In a THz-TDS measurement, thin film samples are grown on substrates transparent to THz as shown in Fig. 2.5c. The sample holder has two apertures for THz signals to pass through (Fig. 2.5a). The THz signal passing through the aperture attached with the sample on a substrate is denoted as “sample” while the THz signal passing through the aperture attached with only a substrate slide is denoted

as “reference”. There is a z -axis stage to control the z -axis position of the sample holder. By controlling the z -axis stage up and down, one can choose to measure the reference and the sample signals (see Fig. 2.5b and Fig. 2.5c). The THz pulses passing through (1) the sample on a substrate [$E_{sam}(t_{\text{THz}})$, Fig. 2.5b] and (2) the substrate [$E_{ref}(t_{\text{THz}})$, Fig. 2.5c] are mapped out at defined time delays t_{THz} . After performing Fourier transformation, the amplitudes of electric fields in the frequency domain for both the sample $E_{sam}(\omega)$ and the reference $E_{ref}(\omega)$ signals can be extracted. The signals contributed by pure sample can be extracted via expression $\frac{E_{sam}(\omega)}{E_{ref}(\omega)}$.

Figure 2.5: (a) Photograph of sample holder with two 3.5-mm apertures for the sample and the reference measurements. Illustration figures for THz signals passing through (c) the sample system and (b) the substrate. White dashed line denotes the aperture positions. Black dashed lines denote the THz beam directions. Black solid arrows show the direction of movement of the z -axis stage.

2.1.2 TRTS setup — 1D and 2D modes

TRTS is THz-TDS with an additional optical pump beam in the setup. Figure 2.6 shows the TRTS setup used in my experiments. The 800-nm laser beam (40 fs, 1 kHz, Coherent Legend Elite) is split into three beams: (1) the optical pump

beam to excite the sample; (2) the THz generation beam; (3) the gating beam to detect THz pulses transmitted through samples. There are two choppers in the setup. One is for the optical pump with working frequency f_{chopper1} , one is for the THz generation beam with working frequency f_{chopper2} . The choppers supply on (off) states by blocking (unblocking) the transmitted laser pulses. The signals collected at photodiodes are sent to two lock-in amplifiers, respectively with reference frequency f_{chopper1} and f_{chopper2} . A lock-in amplifier with f_{chopper1} (f_{chopper2}) can extract signals at frequency f_{chopper1} (f_{chopper2}) with high signal-to-noise ratio.

Figure 2.6: A schematic view of TRTS setup in our lab. The 800-nm beam splits into three: the optical pump beam, the THz generation beam and the THz gating beam. The wavelength of the optical pump beam can be varied from ultraviolet to infrared regions using a combination of and optical parametric amplifier (OPA) and second-harmonic generation (SHG) crystals. The optical pump beam and THz generation beam are modulated by chopper 1 and chopper 2, respectively. The chopper frequencies are controlled by two chopper controllers and then sent to respective lock-in amplifiers as reference inputs. The THz generation and detection parts are included in a dry-air box to exclude the THz absorption of water vapor in ambient air. The optical pump beam can transmit through the hole (denoted by a black dot in the figure) on the parabolic mirror (the one before the cryostat) and then overlaps with the THz beam on the sample surface. A pellicle beam splitter (Pellicle BS) is used to overlap the gating beam and THz beam after the sample. BS denotes the beam splitter.

There are two kinds of modes in TRTS: (1) 1D scan; (2) 2D scan. In the 1D scan mode, using the delay stage in the THz generation beam, one can overlap the gating pulses with the peaks of the THz pulses on the ZnTe detection crystal. By varying

the time delay t_{pp} between the gating pulse and the optical pump pulse using the delay stage in the optical pump beam path, the optical-pump induced change in the transmitted THz electric field $\Delta E(t_{pp})$ from a second lock-in amplifier with f_{chopper2} can be obtained. TRTS in the 1D scan mode is also called as *frequency-integrated* time-resolved spectroscopy because it doesn't have frequency-resolved information. The advantage of 1D TRTS is that the acquisition time takes only several minutes. TRTS in the 2D scan mode is a *time-resolved* frequency-resolved THz spectroscopy. In the 2D scan mode, after using the delay stage in the optical pump beam path to vary the time delay t_{pp} , one can use the delay stage in the THz generation beam path to scan the THz waveform in the time domain, while keeping the pump-probe time delay t_{pp} fixed. During our 2D TRTS measurements, chopper frequency for THz generation beam f_{chopper2} (optical pump beam f_{chopper1}) is 1/2 kHz (1/4 kHz). Therefore, there are four kinds of signals in series in one millisecond, (1) THz-on-pump-on (2) THz-on-pump-off, (3) THz-off-pump-on and (4) THz-off-pump-off. Under this scheme, with the help of lock-in amplifiers, THz electric field $E(t_{\text{THz}})$ and the photoinduced change in THz electric field $\Delta E(t_{\text{THz}})$ as a function of t_{THz} at each pump-probe time delay t_{pp} can be simultaneously detected and collected for further analysis.

2.1.3 Conversion of raw data to conductivity $\tilde{\sigma}(\omega)$ and photoconductivity $\Delta\tilde{\sigma}(\omega)$

THz-TDS data analysis procedures

The flow of THz-TDS data analysis is as shown in Fig. 2.7. Firstly, we obtain the time-domain signals passing through sample system [$E_{\text{sam}}(t_{\text{THz}})$, red line in Fig. 2.7a] and reference substrate [$E_{\text{ref}}(t_{\text{THz}})$, blue line in Fig. 2.7a]. In the case of thin-film sample, at the interface between the thin film and the substrate crystal to grow sample on, the THz pulses are both transmitted and reflected. The backward reflected THz pulse can be totally reflected by the air/sample interface and then hit the sample/substrate interface. The transmitted pulse after a combination of

backward and forward reflections is weaker in amplitude following the main pulse in the time domain (see Fig. 2.7a). The backward and forward reflections can happen again and again until the reflected energy is all dissipated in the sample. The pulses in the time domain following the main pulse are called etalons. The inclusion of etalons in sample analysis leads to artifacts. To extract single-cycle THz pulse passing through the sample system, etalons should be excluded by truncating the time window. Secondly, we obtain both the amplitude and phase of THz frequency-domain signals in Fig. 2.7b [$\tilde{E}_{sam}(\omega)$, red line and $\tilde{E}_{ref}(\omega)$, blue line] by performing the Fourier transformation. Thirdly, we calculate the complex transmittance spectrum $\tilde{T}(\omega)$ via the expression

$$\tilde{T}(\omega) = \frac{\tilde{E}_{sam}(\omega)}{\tilde{E}_{ref}(\omega)}. \quad (2.2)$$

From the transmittance spectra as shown in Fig. 2.7b, we can see a dip at ~ 1.55 THz indicating a phonon mode in the sample. Fourthly, we extract the complex refractive index $\tilde{n}(\omega)$ of the thin film sample from the relation

$$\tilde{T}(\omega) = \frac{2\tilde{n}(\tilde{n}_{sub} + 1)\exp\left[\frac{i\omega d(\tilde{n}-1)}{c}\right]\exp\left[\frac{-i\omega\Delta L(\tilde{n}_{sub}-1)}{c}\right]}{(\tilde{n} + 1)(\tilde{n}_{sub} + \tilde{n}) + (\tilde{n} - 1)(\tilde{n}_{sub} - \tilde{n})\exp\left[\frac{2i\omega d\tilde{n}}{c}\right]}, \quad (2.3)$$

where $\tilde{n}_{sub}$ is the complex refractive index of substrate, d is the thickness of thin film sample, and ΔL is the thickness difference between two substrates for sample and reference. Lastly, we extract the optical conductivity $\tilde{\sigma}(\omega)$ through relations among $\tilde{n}(\omega)$, $\tilde{\epsilon}(\omega)$, and $\tilde{\sigma}(\omega)$ via

$$\begin{aligned} \tilde{\epsilon}(\omega) &= [\tilde{n}(\omega)]^2, \\ \tilde{\epsilon}(\omega) &= \epsilon_{\infty} + i\tilde{\sigma}(\omega)/\epsilon_0\omega, \end{aligned} \quad (2.4)$$

where ϵ_{∞} is the permittivity at high-frequency limit and ϵ_0 is the vacuum permittivity.

Figure 2.7: Left panel: Flow of THz-TDS data analysis. Right panel: (a) Raw data in time domain of thin film sample PbI_2 (red line) and reference (blue line); amplitude (b) and phase (c) after Fourier transformation; (d, e) complex transmittance [(d), amplitude; (e), phase)] obtained via $\tilde{T}(\omega) = \frac{\tilde{E}_{sam}(\omega)}{\tilde{E}_{ref}(\omega)}$; (f, g) real part and the imaginary part of complex refractive index $\tilde{n}(\omega)$ obtained from $\tilde{T}(\omega)$; (h, i) the real part and the imaginary part of complex optical conductivity $\tilde{\sigma}(\omega)$ obtained from complex refractive index. Taken from Ref. [2]

Vacuum–Vacuum measurement Due to fluctuations in the laser power and beam pointing arising from lab temperature fluctuations and electronic noise, the measured THz waveform will contain noise in the data. Before the measurements on samples, vacuum–vacuum (vac–vac) measurements are necessary. Vac–vac measurements are done by measuring THz signals passing through apertures in a vacuum without any sample or substrate. Figure 2.8a shows the vac–vac results ($\frac{E_{sam}(\omega)}{E_{ref}(\omega)}$) obtained from the TPS Spectra 3000 at room temperature with five runs measured in one set. The fluctuation is $\sim 0.5\%$ for each run at frequencies between 0.3 and 3

THz. In this case, as long as the sample contribution is larger than 0.5%, the sample signals are trustable. Figure 2.8b shows temperature-dependent transmittance vac–vac spectra. At different temperatures, as long as we ensure that the THz pulses pass through the center of the apertures on the sample holder, our vac–vac results show that the fluctuations induced by setup is smaller than 0.5%. Our setup is then ready for measurements on real samples.

Figure 2.8: Vac–vac results: (a) Typical vac–vac measurements with 7-mm apertures and (b) temperature dependent vac–vac measurements.

Given issues like absorption of THz photons by cryostat windows, sample holder apertures, and substrate crystals like sodium chloride (NaCl), the real trustable THz ranges will differ from case to case and sample to sample. Therefore, vac–vac measurement are absolutely crucial before THz-TDS and TRTS measurements.

1D-TRTS data analysis procedures In halide perovskite thin films, one can use 1D-TRTS to obtain recombination rate constants, which are rate constants scaled by the quantum yield ϕ . The factor ϕ is defined via the expression

$$\phi = N_0/N_{ph}, \quad (2.5)$$

where N_0 is the initial photogenerated charge carrier density and N_{ph} is the absorbed photon density. The free carrier density $N(t_{pp})$ is related to transient change in

transmission of THz probe pulse $-\frac{\Delta E(t_{pp})}{E(t_{pp})}$ via the relation

$$N(t_{pp}) = \phi N_{ph} \frac{-\Delta E(t_{pp})/E(t_{pp})}{-\Delta E_0/E_0}, \quad (2.6)$$

where the factor $-\Delta E_0/E_0$ is $-\frac{\Delta E(t_{pp})}{E(t_{pp})}$ at $t_{pp} = 0$. Here $t_{pp} = 0$ is defined at the point with the maximum $-\frac{\Delta E(t_{pp})}{E(t_{pp})}$.

The absorbed photon density N_{ph} is given by

$$N_{ph} = \frac{E_{pump} \lambda \alpha(\lambda)}{h c A_{eff}} (1 - R_{pump}), \quad (2.7)$$

where E_{pump} is the pump pulse energy, λ is the pump pulse wavelength, $\alpha(\lambda)$ is the absorption coefficient at λ , h is the Planck's constant and c the speed of light in vacuum, A_{eff} is the pumped area on the sample, and R_{pump} is the reflectance and transmittance at λ of the sample.

If we define $\psi(t_{pp}) \equiv \frac{N_{ph}}{\Delta E(t_{pp})/E(t_{pp})}$ and $x(t_{pp}) \equiv \frac{-\Delta E(t_{pp})}{E(t_{pp})}$, Eq. 2.6 can be rewritten as

$$N(t_{pp}) = \phi \psi(t_{pp}) x(t_{pp}). \quad (2.8)$$

Charge carrier recombination kinetics can be modeled by the rate equation

$$\frac{dN(t_{pp})}{dt_{pp}} = -k_3 N(t_{pp})^3 - k_2 N(t_{pp})^2 - k_1 N(t_{pp}), \quad (2.9)$$

where k_1 , k_2 , and k_3 are the monomolecular, bimolecular, and the third-order Auger rate constant, respectively.

Substituting Eq. 2.8 into Eq. 2.9, one can obtain

$$\frac{dx(t_{pp})}{dt_{pp}} = -\phi^2 \psi^2 k_3 x(t_{pp})^3 - \phi \psi k_2 x(t_{pp})^2 - k_1 x(t_{pp}). \quad (2.10)$$

We can see that if we want to extract recombination rate constants from 1D-TRTS data, the extracted rate constants are scaled by ϕ , i.e., $\phi^2 \psi^2 k_3$, $\phi \psi k_2$, and k_1 . These scaled values are only lower limits of recombination rate constants.

After photoexcitation, in a thin metallic film grown on an insulating substrate $[|\tilde{n}(\lambda_{THz})|d \ll \lambda_{THz}]$ in which $n(\lambda_{THz})$ is the refractive index of the thin film at corresponding wavelength], the photoinduced change in DC conductivity $\Delta\sigma_{DC}(t_{pp})$ is proportional to $\Delta E(t_{pp})/E(t_{pp})$

$$\Delta\sigma_{DC}(t_{pp}) = -\epsilon_0 \frac{c}{d} (1 + n_{sub}) \frac{\Delta E(t_{pp})}{E(t_{pp})}, \quad (2.11)$$

where ϵ_0 is the vacuum permittivity, d is the sample thickness, and n_{sub} is the real part of complex refractive index of the substrate.

From the relation between $\Delta\sigma_{DC}(t_{pp})$ and mobility $\mu(t_{pp})$

$$\Delta\sigma_{DC}(t_{pp}) = eN(t_{pp})\mu(t_{pp}), \quad (2.12)$$

where e is the elementary charge. we can combine Eq. 2.8, 2.11 and 2.12, to obtain a scaled carrier mobility $\phi\mu$ via

$$\phi\mu = \frac{\epsilon_0 c}{ed\phi} (1 + n_{sub}). \quad (2.13)$$

The carrier diffusion length L_D can be determined from the effective carrier mobility μ_{eff} and total recombination rate constants R_{total} via the equation

$$L_D = \sqrt{D/R_{total}} = \sqrt{\mu_{eff} k_B T / e R_{total}}, \quad (2.14)$$

where D is the diffusion constant obtained via $D = \frac{\mu k_B T}{e}$, R_{total} is obtained via $R_{total} = -\frac{1}{N(t)} \frac{dN(t)}{dt}$, and μ_{eff} in 1D TRTS analysis is $\phi\mu$.

Through 1D TRTS analysis, we can only obtain scaled quantities N/ϕ , $\phi\mu$, and $\sqrt{\phi}L_D$. In halide perovskites, the combination of phonon anharmonicity and large photoinduced ionic displacement cause a shift in the lowest-lying phonon mode upon photoexcitation. To accurately obtain N , μ , L_D , and lowest-lying phonon mode dynamics, we can perform 2D-TRTS instead.

2D-TRTS data analysis procedures Figure 2.9a shows the obtained 1D TRTS data at a series of pump–probe time delay $t_{pp,m}$, where m denotes the m^{th} time delay selected from the 1D TRTS scan. From the 1D-TRTS trace, we select a few pump–probe delays to take 2D-TRTS data including one before time zero, e.g., -5 ps (i.e. time delay $t_{pp,static}$) as shown in the inset figure in Fig. 2.9a. One can perform 2D-TRTS analysis as follows: (1) Obtain the time domain signals for sample and reference at equilibrium, [i.e. E_{static}^{sam} and E_{static}^{ref} in Fig. 2.9b], (2) extract the real part and the imaginary part of the optical conductivity at equilibrium (Fig. 2.9c, $\sigma_{1,static}$, $\sigma_{2,static}$) following THz-TDS analysis procedures, (3) extract the real part and the imaginary part of the optical conductivity after photoexcitation $\sigma_{1,t_{pp,m}}(\omega)$ and $\sigma_{2,t_{pp,m}}(\omega)$ at different time delays $t_{pp,m}$; (4) calculate the photoinduced change in both real and imaginary part of the optical conductivity (i.e. photoconductivity) $\Delta\sigma_{1,t_{pp,m}}(\omega)$ and $\Delta\sigma_{2,t_{pp,m}}(\omega)$ via the equations described in Fig. 2.9g.

The extracted $\sigma_1(\omega)$ and $\sigma_2(\omega)$ from THz-TDS measurements and $\Delta\sigma_{1,t_{pp,m}}(\omega)$, $\Delta\sigma_{2,t_{pp,m}}(\omega)$ from TRTS measurements can be used in further analysis to explore the dynamics of carriers, excitons, and phonons.

2.1.4 Physical models to analyze optical conductivity and photoconductivity

After photoexcitation, free carriers, excitons, and phonons can contribute to the measured signals [1,11]. We list here models to describe the response of free carriers, excitons, phonon modes, and plasmons to electromagnetic radiation.

Drude model The Drude model is used to describe free-carrier response in metals and semiconductors. In an applied electric field, the carriers follow

$$m_0 \frac{d^2 \mathbf{r}}{dt^2} + m_0 \gamma \frac{d\mathbf{r}}{dt} = -e\mathbf{E}(t), \quad (2.15)$$

where m_0 is the effective mass of carriers, $\mathbf{r}$ is the displacement of a carrier, $\mathbf{E}(t)$ is the applied electric field [$\mathbf{E}(t) = \mathbf{E}_0 \exp(-i\omega t)$, $\mathbf{E}_0$ is the amplitude of electric field]

Figure 2.9: Left panel: Flow of TRTS data analysis. Right panel: (a) The time delays t_{pp} used in 2D TRTS are chosen from time delays in 1D TRTS. Inset figure shows selected time delay $t_{pp,m}$ and $t_{pp,static}$ for 2D TRTS measurement on a mixed-cation mixed-halide perovskite thin film $FA_{0.85}Cs_{0.15}Pb(I_{0.97}Br_{0.03})_3$ (FCPIB). (b) The electric field signals in time domain for sample and reference at equilibrium show both amplitude and phase differences due to THz absorption by the sample system. Optical conductivity at (c) equilibrium and (e) $t_{pp,m}$ can be extracted following THz-TDS analysis. (d) The photoexcitation induces change in THz electric field $\Delta E_{t_{pp,m}}$ which has expression as $\Delta E_{t_{pp,m}} = E_{t_{pp,m}}^{sam} - E_{static}^{sam}$. (f) The optical conductivity at equilibrium can be seen as reference to see the photoinduced change in optical conductivity at $t_{pp,m}$. (g) The complex photoconductivity at time delay $t_{pp,m}$ can then be calculated via $\Delta\sigma_{1,t_{pp,m}}(\omega) = \sigma_{1,t_{pp,m}}(\omega) - \sigma_{1,static}$ and $\Delta\sigma_{2,t_{pp,m}}(\omega) = \sigma_{2,t_{pp,m}}(\omega) - \sigma_{2,static}$. Taken from Ref. [2]

and γ is the scattering rate.

The relation between the momentum of carriers $\mathbf{P}(t)$ and the displacement $\mathbf{r}$ follows

$$\mathbf{P}(t) = m_0 \frac{d\mathbf{r}}{dt}. \quad (2.16)$$

Hence, substituting Eq. 2.16 into Eq. 2.15 gives

$$\frac{d\mathbf{P}(t)}{dt} = -e\mathbf{E}(t) - \gamma\mathbf{P}(t). \quad (2.17)$$

Using Eq. 2.17, one can obtain expression of $\mathbf{P}(t)$ under an AC electric field

$$\begin{aligned}\mathbf{P}(t) &= \mathbf{P}_0 \exp(-i\omega t), \\ \mathbf{P}_0 &= \frac{e\mathbf{E}_0}{i\omega - \gamma}.\end{aligned}\tag{2.18}$$

Substituting Eq. 2.18 into relation $\mathbf{J}(t) = -Ne\mathbf{v}(t)$, the current density $\mathbf{J}$ is then given as

$$\mathbf{J}(t) = -\frac{Ne\mathbf{P}(t)}{m_0} = \frac{Ne^2}{m_0} \frac{1}{\gamma - i\omega} \mathbf{E}(t)\tag{2.19}$$

where N is the carrier density.

The current density $\mathbf{J}(t)$ and electric field $\mathbf{E}(t)$ is related by

$$\mathbf{J}(t) = \tilde{\sigma} \mathbf{E}(t),\tag{2.20}$$

where $\tilde{\sigma}$ is the complex conductivity.

By combining Eq. 2.19 and 2.20, the complex conductivity $\tilde{\sigma}$ in the Drude model is

$$\tilde{\sigma}_D(\omega) = \frac{\sigma_{DC}}{1 - i\omega\tau_{scat}} = \frac{\epsilon_0\omega_p^2}{\gamma - i\omega},\tag{2.21}$$

where τ_{scat} is the inverse of scattering rate (i.e. $\tau_{scat} = \frac{1}{\gamma}$), σ_{DC} is the DC conductivity ($\sigma_{DC} = \frac{Ne^2\tau_{scat}}{m_0}$), and ω_p is the plasma frequency related to the carrier density N via

$$\omega_p^2 = \frac{Ne^2}{\epsilon_0 m_0}.\tag{2.22}$$

Given the relation between the complex conductivity $\tilde{\sigma}_D(\omega)$ and the dielectric function $\tilde{\epsilon}_D(\omega)$

$$\tilde{\epsilon}_D(\omega) = \epsilon_\infty + \frac{i\sigma_D(\omega)}{\epsilon_0\omega},\tag{2.23}$$

the Drude response in the dielectric function $\tilde{\epsilon}_D(\omega)$ can then be derived via the expression

$$\tilde{\epsilon}_D(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}.\tag{2.24}$$

For a typical Drude conductivity response, there are features as shown in Fig.

2.10 (red line): (1) at 0 THz, $\text{Re}(\tilde{\sigma})$ is at its maximum value σ_{DC} , while $\text{Im}(\tilde{\sigma})$ is at zero. (2) $\text{Re}(\tilde{\sigma})$ and $\text{Im}(\tilde{\sigma})$ cross at $\omega/\gamma = 1$ at the value of $\sigma_{DC}/2$. (3) $\text{Re}(\tilde{\sigma}) \rightarrow 0$ at very high frequencies.

Figure 2.10: Typical complex conductivity spectra in THz region for the Drude model (red solid line, the real part of conductivity $\tilde{\sigma}_{D,1}$; red circle dot, the imaginary part of conductivity $\tilde{\sigma}_{D,2}$) and the Lorentz model (blue solid line, the real part of conductivity $\tilde{\sigma}_{L,1}$; blue circle dot, the imaginary part of conductivity $\tilde{\sigma}_{L,2}$). Assume that in the Lorentz model, $\omega_0 = 5\gamma$, where ω_0 is the angular frequency, (i.e., $\omega_0 = 2\pi f_0$, f_0 is frequency).

Using the Drude model to fit the obtained complex conductivity spectra, one can extract parameters ω_p and γ simultaneously. If the effective mass of carriers m_0 is known, one can then calculate: (1) carrier mobility $\mu = \frac{e}{m_0\gamma}$, (2) carrier density N via $\omega_p^2 = \frac{Ne^2}{\epsilon_0 m_0}$, (3) DC conductivity $\sigma_{DC} = \frac{Ne^2}{m_0\gamma}$.

Lorentz model Peaks of the real part of complex conductivity, $\text{Re}[\tilde{\sigma}(\omega)]$, at finite frequency may be contributed by plasmon, excitons, and phonons [12–14]. The Lorentz oscillator is the simplest model to describe resonances at finite frequencies. When an electron experiences additional force $m_0\omega_0^2\mathbf{r}$, the motion of the electron can be described by

$$m_0 \frac{d^2\mathbf{r}}{dt^2} + m_0\omega_0^2\mathbf{r} + m_0\gamma \frac{d\mathbf{r}}{dt} = -e\mathbf{E}(t), \quad (2.25)$$

where γ is the damping rate.

The corresponding polarization of single electron $\mathbf{P}(t)$ can be expressed as

$$\begin{aligned}\mathbf{P}(t) &= \mathbf{P}_0 \exp(-i\omega t), \\ \mathbf{P}_0 &= \frac{i\omega e \mathbf{E}_0 / m_0}{\omega_0^2 - \omega^2 - i\gamma\omega}.\end{aligned}\tag{2.26}$$

Similar to procedures described in the Drude model, the current $\mathbf{J}$ in the Lorentz model is

$$\mathbf{J}(t) = -\frac{Ne d\mathbf{P}(t)}{m_0 dt} = \frac{-iNe^2\omega \mathbf{E}(t)/m_0}{\omega_0^2 - \omega^2 - i\gamma\omega}.\tag{2.27}$$

The complex conductivity $[\tilde{\sigma}_L(\omega)]$ and dielectric function $[\tilde{\epsilon}_L(\omega)]$ in the Lorentz model can then be

$$\begin{aligned}\tilde{\sigma}_L(\omega) &= -i\epsilon_0\omega(\epsilon_\infty - 1) + \frac{\epsilon_0\omega_L^2\omega}{\gamma\omega + i(\omega_0^2 - \omega^2)}, \\ \tilde{\epsilon}_L(\omega) &= \epsilon_\infty + \frac{\omega_L^2}{\omega_0^2 - \omega^2 - i\gamma\omega},\end{aligned}\tag{2.28}$$

where ω_L^2 is the oscillator strength and ϵ_∞ is the permittivity contributed by dielectric response beyond our frequency window.

The Lorentz model described above is a simple model to characterize a resonance at a finite frequency as shown in Fig. 2.10 (blue line). It has features: (1) real part of complex conductivity ($\tilde{\sigma}_{L,1}$, as defined in Fig. 2.10) is symmetric to $\omega = \omega_0$ with full width at half maximum (FWHM) equal to the damping rate γ , and the imaginary part of complex conductivity $\tilde{\sigma}_{L,2}$ shows a dip following by a peak; (2) at resonance frequency ω_0 , $\tilde{\sigma}_{L,1}$ reaches its maximum value while $\tilde{\sigma}_{L,2}$ crosses zero.

By Lorentz fits to complex conductivity spectra, the resonance frequency ω_0 , damping rate γ , oscillator strength ω_L^2 , epsilon infinity ϵ_∞ can be extracted simultaneously. The extracted ω_0 and damping rate γ are in units of angular frequency, we divide the values by a factor 2π to obtain the values in the unit of frequency.

If more than one Lorentz oscillator contribute to the complex conductivity, the

corresponding $\tilde{\sigma}_L(\omega)$ and $\tilde{\epsilon}_L(\omega)$ can then be derived as

$$\begin{aligned}\tilde{\sigma}_L(\omega) &= -i\epsilon_0\omega(\epsilon_\infty - 1) + \sum_j \frac{\epsilon_0\omega_{Lj}^2\omega_j}{\gamma_j\omega + i(\omega_{0j}^2 - \omega^2)}, \\ \tilde{\epsilon}_L(\omega) &= \epsilon_\infty + \frac{\omega_{Lj}^2}{\omega_{0j}^2 - \omega^2 - i\gamma_j\omega},\end{aligned}\tag{2.29}$$

where ω_{0j} , γ_j , and ω_{Lj} are respectively the resonance angular frequency, the damping rate, and the oscillator strength for the j^{th} Lorentz oscillator.

Peak-Shift model: The Peak-Shift model was first described by Zhao *et al.* to characterize the photoinduced changes in the Lorentz oscillators [11]. This model accounts for the phonon mode contribution to the photoconductivity due to photoexcitation. When the phonon resonance profile is perturbed, the photoinduced change in the complex optical conductivity, or photoconductivity, $\Delta\tilde{\sigma}_{PS}$, can be expressed as a first-order differential to the Lorentzian function

$$\Delta\tilde{\sigma}_{PS}(\omega) = \frac{\partial\tilde{\sigma}_L}{\partial\omega_{Lj}^2}\Delta\omega_{Lj}^2 + \frac{\partial\tilde{\sigma}_L}{\partial\omega_{0j}}\Delta\omega_{0j} + \frac{\partial\tilde{\sigma}_L}{\partial\gamma_j}\Delta\gamma_j,\tag{2.30}$$

where $\Delta\omega_{Lj}^2$, $\Delta\omega_{0j}$, $\Delta\gamma_j$, are the photoinduced changes in ω_{Lj}^2 , ω_{0j} , γ_j , respectively.

After evaluating the differential and assuming a constant damping rate γ_j , the photoconductivity contribution due to the phonon modes is given by

$$\Delta\tilde{\sigma}_{PS}(\omega) = \sum_j \left[\frac{\epsilon_0\omega}{i(\omega_{0j}^2 - \omega^2) + \omega\gamma_j} \Delta\omega_{Lj}^2 + \frac{-2i\omega_j\epsilon_0\omega_{Lj}^2\omega}{[i(\omega_{0j}^2 - \omega^2) + \omega\gamma_j]^2} \Delta\omega_j^2 \right] - i\epsilon_0\omega\Delta\epsilon_\infty.\tag{2.31}$$

The constant damping rate assumption is a phenomenological one, as it does not alter the quality of fit.

Figure 2.11 illustrates the cases where the photoexcitation causes a change in: (1) only the oscillator strength $\Delta\omega_{Lj}^2$ [i.e. height shift in Fig. 2.11a and Fig. 2.11d], (2) only the phonon mode frequency $\Delta\omega_{0j}$ [i.e. frequency shift in Fig. 2.11b and Fig. 2.11e], and (3) both phonon mode amplitude and frequency shift in Fig. 2.11c and Fig. 2.11f. The simulations show that the Peak-Shift model can capture the

photoinduced changes in both phonon mode frequency and amplitude that we see in our data. Using the Peak-Shift model thus enables us to fit the photoconductivity spectra to obtain the changes in phonon mode frequency $\Delta\omega_{0j}$ and oscillator strength $\Delta\omega_{Lj}^2$.

Figure 2.11: Simulations of the Peak-Shift model. The simulated complex optical conductivity spectra $\tilde{\sigma}(\omega)$ (black lines) before pump with (a) a change in phonon mode frequency, (b) a change in height, and (c) a combination of phonon mode frequency shift and height shift, give photoconductivity $\Delta\tilde{\sigma}(\omega)$ shown in (d), (e), and (f), respectively. Grey vertical lines denote the phonon mode frequency before pump. Solid lines: Real part of $\tilde{\sigma}(\omega)$ and $\Delta\tilde{\sigma}(\omega)$. Dashed lines: Imaginary part of $\tilde{\sigma}(\omega)$ and $\Delta\tilde{\sigma}(\omega)$. Taken from Ref. [11]

Drude-Smith model: Scattering in disordered system The Drude-Smith model is an extension of the Drude model to describe disorder-induced scattering in metal and semiconductors. The parameter c_p is introduced to account for the fraction after p scattering events with its velocity still remaining the same. If we define the scattering angle as θ , c_p is also represented as an expectation value $\langle \cos\theta \rangle$ [15,16]. In the Drude-Smith model, the complex conductivity is given as

$$\tilde{\sigma}_{DS}(\omega) = \left(1 + \sum_{p=1}^{\infty} \frac{c_p}{(1 - i\omega\tau_{scat})^p}\right) \tilde{\sigma}_D, \quad (2.32)$$

where $\tilde{\sigma}_D(\omega)$ is the complex conductivity in the Drude model.

The case $c_p = 0$ corresponds to the case where the momentums of carriers are randomly distributed, then the Drude-Smith model reduces to the Drude model.

The case $p = 1$ corresponds to the carriers retaining part of its momentum during the first scattering event. Usually, the series is truncated at $p = 1$. For the case $c_1 = -1$, the carrier is completely backscattered.

Using the Drude-Smith model to fit the complex conductivity, we can extract the disorder factor c_1 , scattering rate γ , and the plasma frequency ω_p . Therefore, using the Drude-Smith model, one can calculate (1) carrier density N from the plasma frequency and (2) the effective carrier mobility via

$$\mu_{eff} = (1 + c_1)\mu, \quad (2.33)$$

where the carrier mobility μ has been described in the Drude model.

Whether the complex conductivity spectra show the responses of the Drude model or the Drude-Smith model, one can obtain carrier density from extracted plasma frequency as described above. The recombination constants can then be extracted using the rate equation to fit the carrier density N . Therefore, through 2D TRTS analysis, one can obtain the quantities N , μ , and recombination constants.

Plasmon model: Plasmon resonance Plasmon resonance is a many-body effect resulting in a coherent oscillation of all electrons, i.e., longitudinal oscillation of the charge in the plasma near the plasma frequency. At interfaces where scattering exists, the coupling of plasmon with a transverse electric field can occur. The applied electric field displaces the electrons and holes in different directions, and the separated charges accumulate at the particle boundaries to form a charge layer at the surface. The resulting dipole moments then correspond to an additional force on the carriers [1]. Similar to that in the Lorentz model, the expression of motion of electron has an additional term $m_0\omega_{pl}^2$ on the left-hand side of Eq. 2.25.

Compared to the Drude model, the complex optical conductivity in the plasmon model is given by

$$\tilde{\sigma}_{PL}(\omega) = \frac{Ne^2\tau_{pl}/m_0}{1 - i\omega\tau_{pl} [1 - (\omega_{pl}^2/\omega^2)]} = \frac{-iNe^2\omega/m_0}{\omega_{pl}^2 - \omega^2 - i\gamma_{pl}\omega}, \quad (2.34)$$

where τ_{pl} is the inverse of the damping rate γ_{pl} and ω_{pl} is a geometrical-dependent parameter linked to the plasma frequency by $\omega_{pl}^2 = f\omega_p^2$ [16]. When the particles in semiconductors are spherical, $f=1/3$.

With $c_p = -1$ and $c_{p>1} = 0$, the Drude-Smith model is reduced to

$$\tilde{\sigma}_{DS}(\omega) = \frac{-i\omega\epsilon_0\omega_p^2}{\gamma^2 - \omega^2 - 2i\omega\gamma}, \quad (2.35)$$

where γ is the scattering rate (i.e., $\gamma = 1/\tau_{scat}$, with τ_{scat} being the scattering time in the Drude-Smith model.). Note that τ_{scat} and τ_{pl} are scattering times in the Drude-Smith model and the plasmon model, respectively. The Drude-Smith model and the plasmon model share the same expression under the conditions [16]

$$\begin{aligned} \omega_{pl}^2 &= 1/\tau_{scat}^2, \\ 1/\tau_{pl} &= 2/\tau_{scat}. \end{aligned} \quad (2.36)$$

In these conditions, the Drude-Smith model under the conditions ($c_p = -1$ and $c_{p>1} = 0$) can be described by the equation of motion of a damped, driven simple harmonic oscillator, which is the same as the plasmon model [16, 17].

2.2 TA: setup and data processing

Compared to TRTS, TA is based on the optical-pump white-light continuum probe principle. In a typical TA measurement, the white-light probe can detect absorption by free carriers and excitons upon photoexcitation [18, 19].

2.2.1 TA: experimental setup

A typical TA setup is shown in Fig. 2.12. The fs-laser beam is split into two: one to pump the sample, another for white-light continuum generation (WLG). In the pump beam path, optical parametric amplifiers (OPA) and second-harmonic generation (SHG) crystals can be used to change the pump pulse wavelength. A

delay stage in the probe beam path is used to control the time delay τ between the pump pulse and the WLG pulse. WLG pulses can be generated with the help of nonlinear crystals like sapphire and calcium fluoride (CaF_2) covering the range from ultraviolet (UV) to mid-infrared (MIR). The neutral density (ND) filter, iris, and lens before the WLG crystals are optics to control the pump power and beam diameter on the nonlinear crystals. Detailed information is described in the following sections. The WLG pulses and the pump pulses overlap at the sample surface. The WLG pulses transmitted through the sample are detected by a detecting system including a monochromator and a photodiode detector. Polarizers ensure the pump beam and the WLG beam have orthogonal polarizations during measurement, to get rid of contributions from the pump beam in the signal [18]. A chopper synchronized to the amplified laser in the pump beam path can mechanically block the laser beam at every other pulse. Therefore, the detecting system can detect sample states with and without laser pulse excitation which can be expressed as $I(\lambda, \tau)_{on}$ and $I(\lambda, \tau)_{off}$, respectively, as a function of wavelength λ and time delay τ (on and off states in subscripts denote states with and without excitations). This detecting mode is denoted as **single-channel mode**. Corresponding intensity spectra as a function of energy can be expressed as $I_{on}(\hbar\omega, \tau)$ and $I_{off}(\hbar\omega, \tau)$ where $\hbar\omega$ is the probe energy.

Given the intensity spectra passing through sample and reference, the absorbance $A(\hbar\omega)$ is defined from the Beer-Lambert law

$$A(\hbar\omega) = \log_{10} \frac{I_i(\hbar\omega)}{I_t(\hbar\omega)}, \quad (2.37)$$

where $I_i(\hbar\omega)$ is the intensity of the incident light and $I_t(\hbar\omega)$ is the transmitted light intensity.

The transient change in absorption induced by the laser excitation at pump-probe time delay τ [$\Delta A(\hbar\omega, \tau)$] can be obtained from

$$\Delta A(\hbar\omega) = \log_{10} \frac{I_i(\hbar\omega, \tau)}{I_{on}(\hbar\omega, \tau)} - \log_{10} \frac{I_i(\hbar\omega, \tau)}{I_{off}(\hbar\omega, \tau)}, \quad (2.38)$$

Figure 2.12: A typical TA setup is shown in this figure. The fs-pulse laser beam is split into one pump beam and one WLG beam. The pump pulse and the white-light continuum probe pulse overlap at the sample surface. After transmitting through the sample system, the white-light continuum probe beam is detected by the detector system enclosed with a spectrometer and a photodiode-detector. R = polarization rotator. RR = retro reflector. # = shutter. mp ($p = 1, 2$) = parabolic mirror. M = mirror (pump path). m = mirror (probe path). L_a = achromatic lens. BS = beam splitter. Modified figure based on Ref. [20].

where $I_i(\hbar\omega, \tau)$ is the incident light at time delay τ . The measured $\Delta A(\hbar\omega, \tau)$ can then be derived as

$$\Delta A(\hbar\omega, \tau) = \log_{10} \frac{I_{off}(\hbar\omega, \tau)}{I_{on}(\hbar\omega, \tau)}. \quad (2.39)$$

Therefore, the transient absorption data $[\Delta A(\hbar\omega, \tau)]$ is a 2D matrix, where the row data correspond to $\Delta A(\hbar\omega)$ at a particular time delay τ , and the column data correspond to the kinetic traces $\Delta A(\tau)$ at a particular probe energy $\hbar\omega$.

The TA system has an optional reference arm in which the white-light continuum beam is split into a reference beam and a probe beam [21]. The reference pulse and the probe pulse are then focused onto the corresponding detecting systems. This measurement scheme is denoted as **signal–reference mode**. While one arm is

transmitting through the sample, the other arm can directly monitor the fluctuations in the probe intensity. The transient absorption in the sample can be derived as

$$\Delta A(\hbar\omega) = \log_{10} \frac{I_{off}(\hbar\omega, \tau)}{I_{on}(\hbar\omega, \tau)} \frac{I_{on,ref}(\hbar\omega, \tau)}{I_{off,ref}(\hbar\omega, \tau)}, \quad (2.40)$$

where $I_{on,ref}(\hbar\omega, \tau)$ is the intensity spectra at time delay τ with laser excitation on measured at reference arm, and $I_{off,ref}(\hbar\omega, \tau)$ is the intensity spectra at time delay τ with laser excitation on measured at the reference arm. The ratio between the intensity spectra measured at two arms [i.e. $\frac{I_{off}(\hbar\omega, \tau)}{I_{on}(\hbar\omega, \tau)} \frac{I_{on,ref}(\hbar\omega, \tau)}{I_{off,ref}(\hbar\omega, \tau)}$] can subtract the effect induced from probe intensity fluctuations [22]. Hence, for a $\Delta A(\hbar\omega, \tau)$ measurement, compared to the single-channel mode, the signal-reference mode can give signal with a larger signal-to-noise ratio.

With the help of sapphire and CaF_2 , the Helios system offers three WLG modes covering ranges: (1) 320 nm–650 nm; (2) 420 nm–780 nm; (3) 760 nm–840 nm [23]. Collimation of the linear delay stage is realized with the help of beam splitter $BS2$ and a charge-coupled device (CCD) camera as shown in Fig.2.12. By marking the position where the WLG beam hits the CCD, we can track its location whenever the beam path changes to make sure (1) the delay stage is collimated and (2) the probe beam points in the same direction and hits the same position on the WLG crystal.

For a TA measurement, the generation, optimization, and detection of the white-light continuum are important procedures to assure high-quality TA data which will be described in the next section.

2.2.2 Generation, optimization, and detection of white-light continuum

The white-light continuum is a spectral broadening of the incident fs laser in transparent media, arising from fs filamentation generated by the high-power fs laser pulse [24]. The spectra-broadening of a laser pulse's spectrum into a white-light

continuum is also called as supercontinuum [25, 26]. The spectral broadening in a bulk material was first observed in a borosilicate glass sample with high-power 530-nm picosecond-pulse excitation [27]. High power 530-nm photons experience positive and negative frequency shifts in the sample. The frequency-swept photons and laser photons are coupled to the laser field via third-order susceptibility. Based on the four-photon process, parametric emission from 400 to 700 nm was generated [27]. The first fs supercontinuum was generated by focusing intense fs pulses (~ 80 fs) into ethylene glycol jet [25]. Their experiments prove that self-phase modulation playing a prominent role in the generation of supercontinuum, and becomes more important with decreasing pulse duration [25]. Self-focusing was also reported as the predominant mechanism in WLG in condensed media, e.g. fused silicon and NaCl [24, 26]. Mechanisms of self-focusing and self-phase modulation are described in the next part.

Self-focusing and self-phase modulation A laser pulse of high intensity introduces change in the real part of the complex refractive index of a nonlinear material. The change is dependent on temporal and spatial distributions of the laser intensity (I) with $n = n_0 + n_2 I$ where n_0 is the refractive index without pump, n_2 is related to the third-order susceptibility of the material and n is the real part of complex refractive index. The coefficient n_2 is usually positive resulting in an increasing refractive index. Considering the spatial power distribution of a laser pulse, change of the refractive index at the center of the excitation position is larger while change at the edges is smaller. Materials with a spatially varying refractive index can act as a lens and cause the laser beam to self-focus. This phenomenon is called **self-focusing**.

With a time-varying refractive index, the phase of a pulse $[\phi_{nl}(t)]$ in the time domain is then changing following the relation

$$\phi_{nl}(t) = -\frac{\omega_0}{c} n_2 I(t) z, \quad (2.41)$$

where c is the speed of light in vacuum, z is the propagation distance, and $\omega_0 = 2\pi f_0$ with f_0 being the central frequency.

Therefore a time-varying phase imparts an instantaneous frequency change with the expression as

$$\omega(t) = \omega_0 + \delta\omega(t), \quad (2.42)$$

where $\delta\omega(t) = \frac{d}{dt}\phi_{nl}(t)$.

The time-varying frequency gives rise to the spectral broadening of a pulse. This effect is called **self-phase modulation**. For a typical Gaussian laser pulse as shown in Fig. 2.13a, the frequency change has the expression

$$\delta\omega(t) = -2\frac{\omega_0}{ct_p^2}n_2I_0\exp\left(-\frac{t^2}{t_p^2}\right)tz, \quad (2.43)$$

where t_p is the pulse duration of the Gaussian pulse [28]. Self-phase modulation can give rise to spectral broadening as illustrated in Fig. 2.13b. The leading front of the pulse generates a negative frequency shift, while the trailing part generates a positive frequency shift. By experimentally defining a critical power where self-phase modulation occurs, one can turn on and off spectral broadening [29].

Alongside self-phase modulation and self-focusing, multiphoton absorption/ ionization induced free-electron plasma and chromatic dispersion all affect WLG. It is believed that the multiphoton excitation of electrons into the conduction band in the self-focus region results in spectral broadening [26]. To modify fs WLG, various factors like focusing geometry, numerical aperture (NA) before the WLG crystals, and laser power to excite the WLG crystals have been studied [24, 30–32].

Optimization of white-light continuum generation The optimization of focusing geometry can extend the frequency range of white-light continuum spectra. A typical supercontinuum spectrum generated in sapphire is shown in Fig. 2.14 covering wavelength range from 410 nm to the mid-infrared range [32]. The spectral energy density used in this figure is directly proportional to the numbers of photons per spectral interval and pulse [32]. The spectrum as a black line is measured in

Figure 2.13: (a) A typical Gaussian shape pulse and (b) self-phase modulation of the pulse induces frequency shift. Taken from Ref. [28]

a standard working condition by focusing the 800-nm beam onto a 3-mm thick sapphire used in a noncollinear parametric amplifier [33]. The plateau in the visible range arises from the super-broadening with the help of electrons generated from multiphoton absorption which can enhance the self-phase modulation [26,34]. Peaks at ~ 800 nm in the spectra come from self-phase modulation [26]. Extension of the white-light continuum spectrum into the infrared region generated from sapphire can be realized through employing an optimized focusing geometry on the same sapphire plate (green line in Fig. 2.14). With the optimized focusing geometry, the white-light continuum spectrum generated from the Yttrium aluminium garnet (YAG) crystal shows a plateau that is quite similar to the white-light continuum spectra from sapphire.

The Numerical Aperture (NA) is a critical parameter governing the interaction between fs laser pulses and transparent materials [30]. When required, one can vary the NA by limiting the beam size with the help of an iris or changing the refractive index of the lens, resulting in the energy threshold for the white-light continuum to be different. Figure 2.15 shows the energy thresholds in fused silica for WLG and

Figure 2.14: White-light continuum spectra from a 3-mm sapphire and a 4-mm YAG (blue line). Green line represents spectra measured at sapphire working under an optimized focusing condition. Black line represents spectrum measured under a standard operation published earlier. The dashed line at ~ 800 nm denotes the input pulse. YAG crystal shows higher spectral intensity in the wavelength range from $1.1 \mu\text{m}$ to $1.2 \mu\text{m}$ (highlighted with dashed lines and arrows). Taken from Ref. [32]

bulk damage as a function of NA. When NA is larger than 0.07, the threshold of bulk damage is smaller than the threshold of WLG. When NA falls below 0.07, the threshold for WLG is almost constant which is smaller than that of bulk damage.

The laser power used to excite the WLG crystal should not be too large or too small. A power smaller than the WLG threshold cannot activate WLG. A large power may lead to modulated white-light continuum spectra with oscillations (see Fig. 2.16e). The modulation induced by the large power can show up as a double-peaked plasma fluorescence trace (Fig. 2.16d) and a modulated far-field pattern in the outer part (Fig. 2.16f). For pulse power which can generate a smooth white-light continuum spectrum as shown in Fig. 2.16b, there is only filamentation induced by self-focusing [Fig. 2.16a]. The far-field pattern of the white-light continuum emission shows colored rings distributed almost symmetrically along the propagation axis. The colored distribution is contributed by chromatic dispersion. Dubietis *et al.* claimed that multiphoton absorption attenuates the central part, thus leading

Figure 2.15: Energy thresholds for white-light continuum (filled circles) and damage (open circles) in fused silica. Taken from Ref. [30]

to the blurred central part [28]. In contrast, with a larger input pulse energy, the refocusing of the filament occurs, resulting in a double peak as shown in Fig. 2.16d. In a refocusing event, after the first self-focusing, light contained in the ring replenishes the pulse on the propagation axis. The replenished pulse undergoes another self-focusing if its power is larger than the critical power for self-focusing. The refocusing of filament in the WLG crystal leads to a periodic modulation on white-light continuum spectra (Fig. 2.16e) and a modulated far-field pattern (Fig. 2.16f).

2.2.3 Issues faced during my TA measurements

For the Helios system in our lab, the positions of the WLG crystal and lens before the nonlinear crystal are fixed. We can only modify white-light continuum generation through adjusting the (1) laser power to excite the WLG crystal and (2) iris to modify the NA of the lens. In my TA measurements, I also tried to extend the wavelength of white-light continuum spectra using an additional filter between the WLG crystal and the sample. Issues in $A(\hbar\omega)$ measurement using our TA setup are

Figure 2.16: Fluorescence traces of filamentation in a YAG crystal with (a) self-focusing and (d) re-focusing events. (b) and (e) show corresponding white-light continuum spectrum. (c) and (f) show corresponding far-field pattern. Input pulses have energies of 310 nJ for case (a) and 560 nJ for case (b). Taken from Ref. [28]

also described in this section.

Extending white-light continuum spectra using filters In a white-light continuum intensity spectrum, the fundamental 800-nm beam is very bright which will saturate photodiodes if nothing is done. The Helios system typically cuts off the spectra at ~ 760 nm to avoid the 800-nm fundamental part with the help of a digital filter (Blue line in Fig. 2.17). However, in materials where the bandgap lies at ~ 800 nm (i.e. ~ 1.55 eV), e.g., a mixed-cation mixed halide perovskite $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$ (FCPIB) with a bandgap of ~ 790 nm (i.e. ~ 1.57 eV), TA spectra near 790–800 nm need to be taken, and so one must try to decrease white-light continuum spectrum intensity at ~ 800 nm so that photodiodes don't saturate. In my experiments, I put a 760-nm short-pass filter before the sample to attenuate the 800-nm fundamental mode. By tilting the angle of the short-pass filter between the white-light continuum beam and its propagation axis, the spectra

can be extended to the mid-infrared range of ~ 825 nm. An additional iris after the short-pass filter also can decrease the intensity of 800-nm fundamental mode. As a result, in my experiment, with the help of the filter and the iris, the white-light continuum spectrum is finally centered around ~ 730 nm with the sacrifice of intensity in the visible range as shown in Fig. 2.17.

Figure 2.17: Modification to white-light continuum spectra using a short pass filter. The blue line represents white-light continuum provided by the Helios system. The orange line is the measured spectra modified with an additional short pass filter

Single-channel mode stability issue: The Helios system in our lab now can only support the single-channel mode. With the single-channel mode, intensity detection may suffer from stability issues when the beam path length is too long, i.e. ~ 10 m in our lab. With a long beam path, when the retroreflector mirror is at opposite ends of the delay stage, the generated white-light continuum spectra are different as shown in Fig. 2.18. Figure 2.18 demonstrates that the spectra at time delays ≤ 1000 ps have similar profiles while spectra at longer time delay (6000 ps, blue dot dashed line) show a similar profile but with slightly different amplitudes. The differences in intensity spectra may arise from different laser pulse energy distributions used to

excite the WLG crystal at different time delays τ . Note that even if the intensity spectra show intensity stability issue at different τ , $\Delta A(\hbar\omega, \tau)$ will not be affected, whereas absorption spectra $A(\hbar\omega, \tau)$ would be.

Figure 2.18: Averaged white-light continuum intensity spectra of different pump-probe time delay: 10 ps (purple dot line), 100 ps (orange solid line), 1000 ps (red dashed line) and 6000 ps (blue dot dashed line).

Fluctuation issues in $A(\hbar\omega)$ measured using TA setup Steady-state absorption spectra is needed if we want to extract exact physical information in the TA spectra. TA spectra can only give photoinduced change in the physical parameters while steady-state absorption spectra can give the physical parameters in steady-state. That is why Yang *et al.* measured the steady-state absorption spectra before they extract of physical parameters from their TA data [35]. To measure the steady-state absorption spectra at the position where we measured TA data, it is best to use the TA setup itself to measure the steady-state absorption spectra. I tried two methods to measure the steady-state absorption spectra using our TA setup: (1) manually saving the intensity spectra passing through sample and reference crystal and (2) saving the raw intensity spectra data during $\Delta A(\hbar\omega, \tau)$ measurement.

In the methods to measure $A(\hbar\omega)$, the sample crystal and the reference crystal

are attached to the sample holder in a cryostat. The cryostat can be moved up and down manually to let white-light continuum pulses pass through sample and reference crystal separately. The intensity spectra of white-light continuum pulses at a fixed time delay can then be measured to calculate the absorbance spectra via the equation

$$A(\hbar\omega) = \log_{10} \frac{I_{off}(\hbar\omega, \tau)}{I_{on}(\hbar\omega, \tau)}. \quad (2.44)$$

The corresponding spectrum is shown as the black solid line in Fig. 2.19a. Compared to the absorbance spectra obtained through the transmission mode of ellipsometry (red line in Fig. 2.19a taken by my collaborator Dr. Chen Xiaoxuan), the black line shows fluctuations at ~ 820 nm and ~ 730 nm. The fluctuations at ~ 820 nm are contributed by small white-light continuum intensity. The fluctuations at ~ 730 nm may come from fluctuations in the peak intensity at ~ 730 nm as shown in the red line in Fig. 2.19b.

The second method to obtain absorbance is to use pump-on $[I_{on}(\hbar\omega, \tau)]$ and pump-off raw data $[I_{off}(\hbar\omega, \tau)]$ during measurements. One can do this in the Helios by enabling "SaveRawData" to activate the raw data taking processes. There are "pump on" and "pump off" raw data files for each $\Delta A(\hbar\omega, \tau)$ scan. Therefore the corresponding absorbance spectra at a certain pump-probe time delay can be obtained via Eq. 2.44. The calculated absorbance spectrum as shown in Fig. 2.19b shows fluctuations around the central peak in intensity spectra. The data taken with the optional reference mode may cancel the fluctuations and improve the signal-to-noise. As a result, to obtain $A(\hbar\omega)$ with good quality, a flat and stable intensity continuum spectrum is desirable. As a comparison, the $A(\hbar\omega)$ spectra obtained from the transmission mode of ellipsometry are smoother and more reproducible across runs. Hereafter, in my TA analysis, the $A(\hbar\omega)$ is obtained from the transmission mode of the ellipsometry setup.

Figure 2.19: Various absorbance spectra measured using ellipsometer's transmission mode (red line in a) and manually taken data using TA (black line in a). (b) shows absorbance spectra obtained from raw data passing through sample and reference crystal

2.2.4 Data processing: methods to analyze data

A typical TA spectra consists of the following features as schematically shown in Fig. 2.20d:

(1) **Excited-state absorption.** They describe optically-allowed transitions from excited states to even higher excited states. They give a positive photoinduced change in the absorption of the probe photons, i.e. $\Delta A > 0$.

(2) **Ground-state bleaching.** They describe the smaller number of probe transitions from the ground state to excited states, as a result of a smaller number of filled states in the ground state caused by photoexcitation. They give $\Delta A < 0$.

(3) **Stimulated emission.** It is the process of an electron in the excited state dropping to a lower energy state due to the presence of an injected photon, and accompanied by the emission of a photon. These electrons in the lower-energy states are thus able to absorb the incident probe photons, giving $\Delta A < 0$.

(4) **Product absorption.** This refers to any TA responses caused by intermediate-state absorption, thus giving $\Delta A > 0$.

We can visualize the first three processes above using energy diagrams of a sample with a ground state and two excited states (excited state 1 and 2). Figure 2.20a–c show the time evolution of the states before, during and after photoexcitation,

respectively. Before photoexcitation, we have all the electrons residing in the ground state and none in the excited states (see Fig. 2.20a). Upon photoexcitation at $\tau = 0$, the pump photons are absorbed by the electrons in the ground state, resulting in a large population of electrons in excited state 1 (see Fig. 2.20b). At $\tau > 0$, a few possibilities exist: (1) the probe photons promote the electrons in excited state 1 to an even-higher excited state 2 (i.e. excited-state absorption), (2) fewer probe photons are absorbed by the reduced number of electrons in the ground state due to prior photoexcitation (i.e. ground-state bleaching), and (3) the probe photons stimulate the electrons in the excited states to drop down to lower-energy states (i.e. stimulated emission), as shown in Fig. 2.20c. Compared to probe absorption before photoexcitation, ground-state bleaching gives $\Delta A < 0$, stimulated emission gives $\Delta A < 0$, and excited-state absorption yields $\Delta A > 0$ at the appropriate probe photon energies, among these processes, the ground-state bleaching usually yields the largest signal [35].

Figure 2.20: Energy diagrams are shown including: (a) steady-state absorption without pump ($\tau < 0$), (b) upon photoexcitation ($\tau = 0$), and (c) after photoexcitation ($\tau > 0$). Typical TA features are illustrated in (c) and (d) with (1), excited-state absorption (pink area), (2) ground state bleaching (green area), and (3) stimulated emission (dashed line in (c) and blue area in (d)). Black (blue) arrows denote probe (pump) pulses. The pink and yellow solid arrows: photon absorption. The green dashed arrows: photon emission. The solid dots: electrons. The hollow dots: holes.

TA spectra can be contributed by various physical processes occurring in the sample. After bandgap excitation on semiconductor material, the photogenerated free carriers first fill the states at the band edges. As a result of the Pauli exclusion principle, the occupied bandedge states force possible optical transitions appearing with higher energies. This phenomenon is called **phase-space filling** (i.e.

band filling) leading to a blueshift of the optical bandgap and a broadening in the bleaching [36]. In contrast, with above-bandgap excitation, the initial distributions of electrons in conduction band and holes in the valence band is athermal, i.e., does not obey the Fermi-Dirac (FD) distribution, which occurs within tens to hundreds of fs after photoexcitation. After thermalization, they then follow the FD distribution and can be described by the band filling effect [37]. Besides carriers, excitons also form upon photoexcitation. Depending on the density of carriers, the quenching of excitons can lead to a bleaching in the spectra [38]. A bandgap shrinkage (bandgap renormalization, BGR) is considered to be the result of mutual exchange and Coulomb interactions between the injected electrons in the conduction band and the injected holes in the conduction band [39]. The bandgap shift upon photoexcitation can lead to the photoinduced absorption below the bandgap and bleaching near the bandedge in spectra [35, 40]. In conclusion, bleaching in TA spectra can be contributed by (1) quenching of exciton absorption near band-edge, (2) broadening by free carriers due to phase-space filling, and (3) continuum bandgap shift due to the BGR.

To analyze TA spectra, the absorption coefficient $\alpha(\hbar\omega)$ is analyzed here because it is proportional to the absorbance O.D. $[A(\hbar\omega)]$ in a semiconductor with the expression

$$\text{O.D.}(\hbar\omega) = 0.434\alpha(\hbar\omega)l. \quad (2.45)$$

The absorption coefficient α is determined by transition rate $W_{i \rightarrow f}(\hbar\omega)$ between the initial state i and the final state f , with

$$W_{i \rightarrow f}(\hbar\omega) = \frac{2\pi}{\hbar} |M|^2 g(\hbar\omega), \quad (2.46)$$

where M is the transition matrix and $g(\hbar\omega)$ is the joint density of states at the photon energy $\hbar\omega$. In Elliott's theory [41], the absorption spectra can be modeled

by the combination of (1) exciton contribution part (EC),

$$\alpha_{EC}(\hbar\omega) \approx E_b^{\frac{3}{2}} \sum_{j=1}^{\infty} \frac{4\pi}{n^3} \delta(\hbar\omega - E_g + E_b/j^2), \quad (2.47)$$

and (2) carrier contribution part (CC),

$$\alpha_{CC}(\hbar\omega) \approx \theta(\hbar\omega - E_g) D_{CV}(\hbar\omega) \frac{\pi x e^{\pi x}}{\sinh(\pi x)}, \quad (2.48)$$

where E_g is the bandgap, E_b is the exciton binding energy, θ is the step function, $D_{CV}(\hbar\omega)$ is the joint density of states, and $\frac{\pi x e^{\pi x}}{\sinh(\pi x)}$ is an enhanced factor from Coulomb interaction with

$$x = \frac{\sqrt{E_b}}{\sqrt{\hbar\omega - E_g}}. \quad (2.49)$$

The parameters E_b , E_g , and Γ can be obtained through fits to the steady-state absorption spectra using Elliott's formula. Subsequently, taking into account the photoinduced changes in E_b , E_g and Γ , and band filling effect, $\Delta A(\hbar\omega, \tau)$ can be modeled with the expression

$$\Delta A(\hbar\omega, \tau) = A_{pump}(E'_b, E'_g, \Gamma')(1 - f_{FD})^2 - A(E_b, E_g, \Gamma), \quad (2.50)$$

where E'_b , E'_g , and Γ' are the values of the exciton binding energy, the bandgap, and the exciton bandwidth *after* photoexcitation, $f_{FD}(\hbar\omega)$ is the FD distribution with expression

$$f_{FD}(\hbar\omega) = \frac{1}{1 + \exp \frac{\hbar\omega - E_f}{k_B T_e}}, \quad (2.51)$$

where E_f is the Fermi energy, k_B is the Boltzmann constant and T_e is the electron temperature. By fitting $\Delta A(\hbar\omega, \tau)$ with Eq. 2.50, the photoinduced change in the parameters E_b , E_g , and Γ can then be obtained.

The distribution of photogenerated electrons (holes) follows the (FD)distribution of electrons f_e (holes f_q). In lead halide perovskite systems, one can assume that $f_e \approx f_h$ with roughly equal effective masses and quasi-Fermi energies [35]. With

the assumption that the electron density is equal to the hole density, the electron density N_e can then be a measure of carrier density N . The total number density of electrons N_e satisfy

$$N_e(\hbar\omega) = \int_{E_g}^{\infty} g_c(\hbar\omega) f_e(\hbar\omega) d(\hbar\omega), \quad (2.52)$$

where $g_c(\hbar\omega)$ is the density of states in the conduction band [35]. Substituting the extracted parameters from $\Delta A(\hbar\omega, \tau)$ fits into Eq. 2.52, one can obtain the total number density of electrons. Yang *et al.* obtained the carrier density as a function of fluence using Eq. 2.52 after extracting fitting parameters from $\Delta A(\hbar\omega, \tau)$ analysis [35]. Once the carrier density as a function of time delay is obtained, one can (1) obtain the time evolution of carrier density after photoexcitation and (2) use the rate equation (i.e. Eq. 2.9) to fit the electron density $N_e(\tau)$ to unravel the carrier recombination mechanisms.

TRTS is a powerful tool to obtain the density of free carriers, carrier mobilities, and phonon dynamics in halide perovskite systems. Compared to TRTS, TA probes the sample with higher-energy photons. With both steady-state absorption and TA measurements, one can obtain physical information like bandgap E_g , exciton binding energy E_b , Fermi energy E_f , and carrier temperature T_e . TRTS and TA are therefore complementary methods to probe the dynamics of carriers and excitons in a sample.

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Chapter 3

Overview of Lead Halide Perovskites

In this chapter, a overview of perovskite solar cells and their properties will be given. It contains two parts: (1) Lead halide perovskite fundamentals; (2) photophysical properties of lead halide perovskites: why perovskites?

3.1 Lead halide perovskite fundamentals

3.1.1 Perovskite crystal structure

Perovskite structure represents a crystal structure as that of calcium titanate (CaTiO_3), which was first discovered in the Ural mountains by Gustav Rose [1]. A typical lead halide perovskite has a structure formula as ABX_3 , in which the B sites are Pb^{2+} cations, X sites are halide elements like Br^- , I^- , Cl^- , while cation A can be inorganic [e.g., Cs^+ , Rb^+] or organic [e.g., methylammonium (MA^+ or CH_3NH_3^+), formamidinium (FA^+ or CHN_2H_4^+)]. The B and X sites form octahedral structures at the corners of each unit cell. With the A cations as inorganic or organic, the corresponding perovskites are all-inorganic perovskites or hybrid organic–inorganic perovskites (HOIP).

Figure 3.1 shows comparative illustrations of Cs^+ based all-inorganic perovskite

and MA^+ based HOIPs with the same B and X. There is no strong orientational dependence in spherically symmetric Cs^+ while MA^+ shows subtle orientation dependence. With the same B and X elements, different A cations lead to different physical properties in the material [2, 3]. The bandgap of the perovskites can be tuned through cation engineering [2, 4].

Figure 3.1: Perovskite structure APbI_3 with A^+ as (a) inorganic cation Cs^+ and (b) organic cation MA^+ . Compared to the spherically symmetric inorganic Cs^+ , MA^+ shows an orientational dependence. Illustrations of the disorder of MA^+ are presented at the bottom. Modified figure taken from Ref. [2]

3.1.2 Fabrication of halide perovskite thin films

The quality of the perovskite films plays a key role in their photovoltaic performance. Device scientists thus developed elaborate sample growing techniques to enhance the film quality [5]. Perovskite samples were grown via different various growth techniques, such as spin coating and vapor-assisted deposition [6, 7].

Spin coating An amazing feature of the perovskites is that they can exhibit high PCEs via relatively inexpensive solution-processed procedures based on spin coating

[8]. Spin coating is a technique to deposit uniform thin films onto flat substrates, and has been widely used to grow solution-processed perovskite materials. Typically, the coating material is applied onto the center of a substrate. The substrate is then affixed onto a spin coater and rotated to spread the coating material onto the entire substrate. By controlling the amount of coating material, rotating time, and rotation speed of the spin coater, full-coverage thin films with designed thickness are fabricated. For perovskites, the strong ionic interaction between the metal ions and halogen anions results in the formation of well-crystallized perovskite during spinning where the evaporation and convective self-assembly processes take place.

To obtain large-area high-quality films, the optimized fabrication procedures including one-step and two-step spin coating were reported [6, 8, 9]. Guo *et al.* reported a facile one-step spin-coating method assisted with a preheating process to obtain high-quality CsPbI₂Br films. The precursor solutions CsI and PbBr₂ are prepared with molar ratio 1:1 in dimethyl sulfoxide (DMSO). Before spin coating, the SnO₂/ITO substrates were heated with a hot plate for 10 min. Substrate-preheating processes before spin coating accelerate solvent molecule volatilization and hence the crystal growth speed in the precursor films, resulting in the full-coverage and enhanced crystallinity of the CsPbI₂Br films. With the preheating substrates, the PCE (with average value $\sim 9.07\%$) and short-circuit current density $\sim 10.69 \text{ mA cm}^{-2}$) of the obtained perovskite solar cells are enhanced when compared to spin coating without substrate preheating (with average PCE $\sim 6.57\%$ and short-circuit current density $\sim 6.89 \text{ mA cm}^{-2}$) [6]. Im *et al.* obtained MAPbI₃ cuboids with controlled size using a two-step spin coating method. With a first-step spin coating of PbI₂ precursor solution, followed by a second-step spin-coating of MAI solution with a loading time [9]. An excellent PCE of $\sim 17\%$ is obtained from the size-controlled MAPbI₃ cuboids solar cell systems [9].

Vacuum deposition Vacuum deposition is a family of processes used to deposit thin film material atom by atom, or molecule by molecule, on substrates, which has been used to grow high-quality and high-performance solid material [10]. Vacuum

deposition operates at vacuum pressures to form freestanding structures. The processes can be classified into physical vapor deposition (PVD) and chemical vapor deposition (CVD). The common PVD processes are sputtering and evaporation. The CVD technique is a process widely used in industry for the vapor deposition of perovskites. In a typical two-step method of perovskite synthesis via CVD, a precursor powder of metal halide is first converted into the gas phase, followed by the addition of halide salts [7]. The volatile precursors react and then deposit on the substrates. The perovskite films grown by CVD show fewer defects and higher quality than the solution-processed perovskite films [10].

Leyden *et al.* first fabricated perovskite solar cells using CVD [7], and obtained a PCE of as high as 11.8%. The same group also reported a combined synthesis method of CVD and raster ultrasonic spray coating [11]. In contrast with the spin-coating method, this combined method is more environmentally friendly, and exhibited a smaller decrease of PCE with increasing device area [11]. Though thin films obtained with vapor-deposition techniques show full-coverage and uniformity over large areas, the vacuum configuration is needed, which increase fabrication time and cost of making these perovskite solar cells [10].

3.1.3 Halide perovskite solar cells

Compared to traditional fossil energy, solar energy is a promising substitute. According to the efficiency chart as shown in Fig. 3.2, the PCE of solar cells based on inorganic semiconductors, such as silicon (Si), gallium arsenide (GaAs), and copper indium gallium selenide (CIGS) have to date reached over 26% [12]. To reduce product costs and simplify fabrication processes, the search for better photovoltaic material has not stopped. In the 1990s, dye-sensitized solar cells (DSSC) were first fabricated by O'Regan and Grätzel [13]. In a DSSC, a current is generated when the sensitizer (i.e. dye molecules) is photoexcited, followed by electron injection into the conduction band of the mesoporous semiconductor (e.g. TiO_2). The sensitizer is rapidly reduced by a donor species in the electrolyte. Hence, one can complete

the loop to convert solar power into electrons using the DSSC system [13].

Figure 3.2: Best research cell efficiency chart. Taken from Ref. [12]

Halide perovskite based solar cells were first reported by Mitzi *et al.* with their electron-transporting properties [14,15]. Perovskite-sensitized solar cells were initiated by Kojima *et al.* using HOIP-sensitized TiO_2 as the light absorber with PCE of 3.8 % in 2009 [16,17]. In these perovskite-sensitized solar cell systems, perovskites play roles as light absorbers just like what dye molecules do in DSSC [16–18]. However, the perovskites' degradation in the liquid electrolyte limits the efficiency of the solar cell. In 2012, a perovskite-sensitized all-solid-state solar cell was reported by Kim *et al.* with an elevated PCE of 9.7% (Fig. 3.3a) [19]. Typical solid-state perovskite-based solar cells have the form as shown in Fig. 3.3a-c. Figure 3.3b shows the planar heterojunction structure formed with a dense perovskite layer together with an electron-transporting layer (ETL) and a hole-transporting layer (HTL) without the mesoporous structure as shown in Fig. 3.3b. In such structures, the charge carrier diffusion lengths can be very long with $\sim 1 \mu\text{m}$ in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ [20]. HOIPs were reported to possess hole-transporting properties themselves, which enabled the invention of the inverted planar heterojunction structure [21]. The inverted planar heterojunction structure has a fabrication sequence: first the ETL, second the perovskite layer, and then the ETL (see Fig. 3.3c) [8]. In an inverted

planar heterojunction structure, electrons are transferred to the back metal cathode (Al) layer in Fig. 3.3d, while holes would be collected by the transparent conducting anode (indium-doped tin oxide, ITO) layer as shown in Fig. 3.3d. The interface layers among the perovskite layer, the Al layer, and the ITO layer serve to reduce the energy barriers and suppress potential interfacial charge recombination [22].

After the solid-state planar perovskite-based solar cell was invented, intense works had been reported to raise the PCE of perovskite solar cells. Reported methods to raise PCE include: (1) adding carrier extraction layers; (2) suppressing disorder in carrier extraction layers; (3) adopting mixed-cation (mixed-halide) perovskites, etc. [23–25].

Figure 3.3: Schematic illustrations of perovskite solar cells with (a) regular mesoporous structure, (b) regular planar structure, and (c) inverted planar structure. Taken from Ref. [22]

3.1.4 Shockley–Queisser (SQ) efficiencies limit

The PCE of a solar cell system is determined by the short-circuit current density I_{SC} (the current when the solar cell is short circuited), the open-circuit voltage V_{OC} (the

voltage from the solar cell at zero current), and the fill factor FF via the expression

$$PCE = I_{SC}V_{OC}FF/P_{in}, \quad (3.1)$$

where P_{in} is the incident power. The fill factor is defined as the ratio

$$FF = \frac{V_{max}I_{max}}{I_{SC}V_{OC}}, \quad (3.2)$$

where V_{max} (I_{max}) is the voltage (current) at the maximum output power.

To calculate the PCE efficiency limits, Shockley and Queisser made the following assumptions: (1) the solar spectrum can be approximated by the emission of a blackbody with a surface temperature of 6000 K, (2) photons with energy above the bandgap of a solar cell are 100% converted into electron-hole pairs (i.e., quantum efficiency equals 100%), while photons with energy below the bandgap cannot be absorbed by the solar cell material, (3) the only recombination path in the solar cell is radiative recombination. Using Eq. 3.1, they obtained the famous bandgap-dependent Shockley-Queisser (SQ) efficiency limit [26].

Taking into account of the atmosphere and the potential scattering, Seven Rühle modified the SQ efficiency limit under AM 1.5 G spectral irradiance [27]. The integral power density of AM 1.5 G is 1000.4 W/m² while for a blackbody with a surface temperature 6000 K is 1576.7 W/m² [27]. The irradiance spectrum AM 1 can be used to estimate the performance of solar cells in equatorial and tropical regions. The modified SQ efficiency limit is shown as the black solid line in Fig. 3.4. One can see that the SQ limit is largest when the bandgap is at ~ 1.38 eV.

Single-junction perovskite solar cells based on HOIPs can have PCE easily over 20%, e.g., the single-junction perovskite solar cell based on mixed-cation perovskite (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} was reported with a PCE of 22.1% by Yang and his coworkers (see the orange diamond in Fig. 3.4) [28]. PCEs of the solar cells based on the all-inorganic CsPbI_{3-x}Br_x ($x = 0, 1, 2$, and 3) series have not reached their SQ limit yet. Up to now, the highest certified PCE in single-junction perovskite solar

cells is achieved by the KRICT/MIT team [Korea Research Institute of Chemical Technology (KRICT)] [12, 29]. They used a quadruple cation perovskite system as the light-absorbing material and obtained a large PCE of up to 25.2% as shown in Fig. 3.4 [12, 30]. The next section surveys our current understanding of the photophysics of perovskites.

Figure 3.4: Schematic illustration of the SQ efficiency limit. Black line: modified SQ limit [27]. Black square: the highest certified PCE of a quadruple-cation perovskite [29]. Orange diamond: PCE of a mixed-cation perovskite [28]. Green triangle: PCE of CsPbI₃ [31]. Purple pentagon: PCE of CsPbI₂Br [32]. Red circle: PCE of CsPbIBr₂ [33]. Blue star: PCE of CsPbBr₃ [34]

3.1.5 Other applications of halide perovskites

Due to the extraordinary electronic properties which will be discussed in next section, and their facile fabrication processes, halide perovskites have been applied to photovoltaics [35]. The excellent electronic properties also render perovskites very useful in other applications, as shown in Fig. 3.5, such as chemical catalysts [36], lasers [37], x-ray detectors [38], light-emitting diodes [39], and lithium-ion batteries [40].

Lead halide perovskite based photovoltaic devices have been reported to show high PCE, and have been verified as potential materials in photovoltaic devices. The

Figure 3.5: Applications of perovskites: (a) solar cells [35], (b) chemical catalysts [36], (c) lasers [37], (d) X-ray detectors [38], (e) Light-emitting diodes [39], and (f) Lithium-ion batteries [40].

corresponding photophysics of perovskites will be described in the next section.

3.2 Photophysical properties of lead halide perovskites: why perovskites?

So far, it is claimed that the superior perovskite solar cell performance originates from the intrinsic properties in the lead halide perovskites such as large absorption coefficient [41, 42], shallow defect level [43], and small photocarrier effective masses [44]. These intrinsic properties in the lead halide perovskites can be understood through a combination of high perovskite symmetry and unique band structures. In this section, I will introduce the related photophysical properties in the perovskites and their resulting long carrier diffusion length and low recombination rate [41, 45, 46].

3.2.1 Band structure

The unusual band structure in the lead halide perovskite arises from the combination of high symmetry, and the unique atomic electronic configuration of Pb — a lone pair of electrons in the Pb 6s shell [46]. First-principles density functional theory (DFT)

calculations as shown in Fig. 3.6 show that inorganic Pb and I⁻ contribute to the density of states (DOS) mainly near the band edge, while the organic cation MA⁺ contributes to DOS at higher energies. This indicates that the organic cation does not directly determine the basic electronic structure in the halide perovskites [41]. With high symmetry in halide perovskite, the conduction band minimum (CBM) is composed of degenerate Pb *p* bands [41, 47]. The fully occupied Pb(*s*) orbital has strong antibonding coupling with I(*p*) orbital, leading to a dispersive valence band maximum (VBM) as shown in Fig. 3.6a [46]. Dispersive VBM can then result in a small hole effective mass which is comparable to the electron effective mass [46]. Strong spin-orbit interaction (SOC) can also contribute to smaller effective masses in the perovskites [48]. A smaller effective mass leads to a higher carrier mobility, a longer carrier diffusion length, and smaller non-radiative recombination [49].

Figure 3.6: Calculated electronic structure of MAPbI₃. (a) typical band structure; (b) total DOS and partial DOS of (c) cation MA⁺ (d), Pb and (e) I atoms. Taken from Ref. [46]

Figure 3.7a shows the DOS of CsPbI₃ projected on atoms Cs, Pb, and I atoms (partial DOS) obtained from the DFT calculations. Bandedge states of the conduction band (CB) and the valence band (VB) are dominated by Pb and I contributions while the Cs contribution is low. Cs contributes mainly at higher energy of ~ 4

eV. The sharp feature at ~ 8 eV arises from the Cs contribution [50]. Crystal Orbital Hamiltonian Population (COHP) analysis can give covalent bonding and anti-bonding orbital information of the DOS at certain energies [51]. The COHP results from multiplying the DOS by the corresponding element of the Hamiltonian. Hence, one can partition the band structure energy into bonding, nonbonding, and antibonding contributions via COHP calculations. The orbital resolved-COHP curves of CsPbI_3 presented in Fig. 3.7b prove that Cs doesn't participate in covalent bonding [50]. With the hybridization of s and p orbitals of Pb and I atoms, four pairs of bonding/anti-bonding states can be identified as shown in Fig. 3.7b. Comparing Fig. 3.7b and c, the VBM is believed to be a $\text{Pb}(s)\text{--I}(p)$ anti-bonding state while the CBM is a $\text{Pb}(p)\text{--I}(s)$ anti-bonding state. Recently, the concept of electronic dimensionality is defined to account for the connectivity of the electronic orbitals that comprise the lower CB and the upper VB [45, 52]. Though some perovskites are 3D in both structural dimensionality and the electronic dimensionality, some are structurally 3D but exhibiting lower-dimensional electronic dimensionality (e.g., the Ag- and Bi-based double perovskite $\text{Cs}_2\text{AgBiX}_6$ is electronically 0D and structurally 3D) [53]. One can justify the electronic dimensionality of materials via the COHP results. The electronic dimensionality could be a useful concept in estimating the photovoltaic performances.

Band structure: large absorption coefficient A large absorption coefficient also makes lead halide perovskites good candidate materials in solar cell devices. The large absorption coefficient arises from the special band structure in lead halide perovskites. Figure 3.8a shows schematic figures of optical absorption processes in traditional semiconductors silicon (Si), gallium arsenide (GaAs), and MAPbI_3 . Silicon is a first-generation absorber which possesses an indirect bandgap with forbidden direct transitions between band edges. With a direct bandgap, the absorption coefficient can increase by two orders of magnitude [41]. Though GaAs (the second-generation absorber in photovoltaic devices) shows a direct bandgap, the conduction band of GaAs is derived from Ga 4s states, while the conduction band of MAPbI_3

Figure 3.7: (a) Partial DOS and (b) orbital resolved-COHP of CsPbI₃ shows bonding (anti-bonding) character in positive (negative) sign (One should note here -COHP is a negative COHP). (c) shows schematic energy level diagram extracted from the COHP analysis. The position of VBM is set to 0. Blue shaded area denotes the anti-bonding interaction while yellow shaded area denotes the bonding interaction. Taken from Ref. [50]

is mainly from Pb 6p bands which is less dispersive than that in GaAs [41]. As a result, Fig. 3.8b show the DOS of MAPbI₃ to be larger than that in GaAs, especially for photon energy between 0 and 2 eV leading to a higher joint density of states (JDOS) in the corresponding range. As the absorption coefficient is a combination of the transition matrix element and the JDOS, compared to GaAs, the absorption coefficient in the perovskites is up to one order of magnitude higher within the visible light range (Fig. 3.8d) [41, 42] that comprises the major usable portion of the full solar cell spectrum. With a large absorption coefficient within the visible light range, solar cell developers can easily use thin-film perovskite to obtain high PCE (Fig 3.8e). From the perspective of effective mass of carriers, in contrast to the large difference between the effective masses of the electron and the hole in conventional semiconductors like GaAs and Si [54–56], the similar effective mass values of electrons and holes in perovskites lead to a larger absorption cross-section. Hence, perovskites are ideal candidates as light-harvesting materials in solar cell devices.

Figure 3.8: Optical absorption of perovskites, first-generation photovoltaic material Si, and the second-generation photovoltaic material GaAs. (a) Schematic figures of optical absorption by Si, GaAs, and MAPbI₃. (b) DOS and (c) JDOS of both GaAs and MAPbI₃. (d) Absorption spectra of GaAs and MAPbI₃. (e) Maximum efficiency of several materials. Taken from Ref. [49]

Band structure: shallow defect level Lead halide perovskites show excellent defect tolerance. Defect tolerance is used to characterize the stability of electronic properties against defects in materials. Steirer *et al.* reported the electronic structure in perovskite MAPbI₃ changes only with a high concentration of defects [57]. One reason for the high defect tolerance in lead halide perovskite is their shallow defect levels. The properties of point defects can be calculated by DFT calculations. Yin *et al.* calculated all the possible intrinsic point defects in perovskite MAPbI₃ from which defect energy levels can be plotted (Fig. 3.9). Figure 3.9 shows that the dominant defects in MAPbI₃ are shallow while deep defects are few with large formation energy. The shallow defect level in lead halide perovskite originates from the strong Pb lone-pair *s* orbital and I(*p*) orbital antibonding coupling [46, 58].

Lead halide perovskites possess high symmetry and unusual band structure, which result in excellent photovoltaic performance. To explain the photophysical properties underlying the excellent performance, that may later guide device fabricators, various ultrafast techniques are used to study the materials. Ultrafast techniques including TRTS and TA focus on the phonon, carrier and exciton degrees

Figure 3.9: Calculated transition energy levels of point defects in perovskite $MAPbI_3$. The formation energy of each defect is shown in parentheses in black under every defect names. Defect names includes: I_i (I interstitials), MA_{Pb} (MA molecules on Pb sites), V_{MA} (MA vacancies), V_{Pb} (Pb vacancies), I_{MA} (I atoms at MA sites), I_{Pb} (I atoms at Pb sites), MA_i (MA interstitials), Pb_{MA} (Pb atoms on MA), V_I (I vacancies), Pb_i (Pb interstitials), MA_I (MA molecules at I sites), Pb_I (Pb atoms at I sites). The acceptors/donors are listed in the order of formation energies from left to right. Each transition denotation in parentheses (both red and blue color) are defined following published papers in which the numbers denote the number of excess electrons [59]. Taken from Ref. [42]

of freedom after photoexcitation. In the next section, we describe some optical studies of lead halide perovskites.

3.2.2 Phonon modes in lead halide perovskites

In the Lorentz model introduced in Chapter 2, one can extract the resonant angular frequency ω_0 ($\omega_0 = 2\pi f_0$, where f_0 is frequency) and oscillator strength ω_L^2 from Lorentzian fits. La-o-vorakiat *et al.* reported temperature-dependent THz-TDS measurements of $MAPbI_3$ thin film [60]. Figure 3.10a shows the real part of the complex optical conductivity from 20 K to 300 K. At 300 K, there are two phonon modes at ~ 1 THz (low-THz mode) and ~ 2 THz (high-THz mode). DFT calculations showed that the observed phonon modes arise from the Pb-I vibrations near 1 THz

and 2 THz [60, 61]. With the temperature decreasing to 20 K, the two phonon modes split into four phonon modes. The imaginary part of the complex optical conductivity plotted in Fig. 3.10b show dip-peak features, showing that their THz conductivity could be fitted with the Lorentz model.

Figure 3.10: Temperature dependent complex conductivity with Lorentzian response. Solid lines are the Lorentz fits. Dotted lines are data. Taken from Ref. [60]

Using two Lorentzian oscillators to fit the 300-K data and four Lorentzian oscillators to fit the 20-K data, La-o-vorakiat *et al.* extracted Lorentzian parameters including oscillator strength ($\omega_{p,m}^2$), phonon frequency (f_m), and phonon damping rate (Γ_m) of the m^{th} ($m = 1, 2, 3$, and 4) Lorentzian oscillator as plotted in Fig. 3.11. With decreasing temperature, MAPbI₃ experiences a structural phase transition from the tetragonal phase to the orthorhombic phase at ~ 165 K [60]. The extracted parameters show a discontinuity showing clearly the existence of a structural phase transition. The two additional phonon modes at low temperature are believed to originate from the lifting of degeneracy along the a and b axes due to the decrease in crystal symmetry across the tetragonal–orthorhombic phase transition [60].

Given the low energy of the THz pulse, THz-TDS can directly detect the lowest-

Figure 3.11: Temperature-dependent Lorentzian parameters extracted from fits to data. High-THz phonon modes (blue line) and low-THz phonon modes (red line) dynamics as a function of temperature are plotted. Phase transition can be seen clearly at ~ 150 K. Taken from Ref. [60]

lying phonon modes. Ultrafast techniques, e.g. TRTS and TA, can measure the photoinduced change in absorption leading to the extraction of the relevant carrier, phonon and exciton dynamics.

3.2.3 Carriers: band filling and recombination in lead halide perovskites

After photoexcitation, the photogenerated carriers in semiconductors possess excess energies. These carriers then relax towards the bottom of the CB or recombine directly with the assistance of phonon modes or trap states.

In semiconductor-based optoelectronic devices, the recombination of photogenerated carriers is a major loss process. Taking into account of the different recombination channels that decrease the carrier density, the charge carrier recombination

kinetics can be modeled by the rate equation described in Eq. 2.8. The extracted constants k_1 , k_2 , k_3 represent (1) first-order Shockley-Reed (trap state-mediated) recombination, (2) second-order (bi-molecular) recombination, and (3) three-body (Auger-mediated) recombination. These recombination channels may exist together after photoexcitation.

TRTS is an ultrafast technique that can track the carrier density after photoexcitation and hence elucidate the free-carrier recombination kinetics in semiconductors. Using TRTS, the carrier density and mobility after photoexcitation can be extracted. The corresponding diffusion length, recombination constants (k_1 , k_2 , and k_3), and carrier backscattering factor in the thin film can be extracted. La-o-vorakiat *et al.* reported TRTS results on MAPbI₃ thin film measured at different temperatures with 400-nm excitation [62]. The real $[\Delta\sigma_1(\omega)]$ and imaginary $[\Delta\sigma_2(\omega)]$ parts of photoconductivity at 15 K (Fig. 3.12a and b) and 285 K (Fig. 3.12c and d) are shown in Fig. 3.12. The features are consistent with Drude-Smith response considering that free-carrier response in the heavily-disordered thin film is modified by backscattering. The free carrier response (Drude part) and scattering-induced response (Smith part) in Drude-Smith fits are represented by the yellow and red regions.

Using the extracted parameters from the Drude-Smith fits, the carrier density (n) and disorder-induced mobility $[\mu_{eff} = (1 + c_1)\mu]$ as a function of time delay can be obtained (Fig. 3.13). Knowing the carrier density N , the carrier recombination kinetics can then be determined with the help of Eq. 2.9. The fits as shown in Fig. 3.13a-b reveal that the second-order recombination dominates at 285 K while the third-order recombination plays a dominant role at 15 K. The second-order rate constant at 285 K is $k_2 = 2 \times 10^{-8} \text{ cm}^3\text{s}^{-1}$, while at 15 K, the third-order rate constant is $k_3 = 2 \times 10^{-25} \text{ cm}^6\text{s}^{-1}$. These values are consistent with published recombination rates obtained with 1D TRTS results [63]. The disorder-induced effective mobility μ_{eff} at 285 K in Fig. 3.13c reaches its maximum value in 10 ps, while at 15 K, μ_{eff} reaches its maximum value in 20 ps and maintains a larger μ_{eff}

Figure 3.12: Complex conductivity [(a) $\Delta\sigma_1$ and (b), $\Delta\sigma_2$] with Drude-Smith response. The yellow, red regions represent Drude and Smith contributions. Dashed lines and black solid dot lines are the Drude-Smith fits and data. Taken from Ref. [62]

than that at 285 K. These results suggest the MAPbI₃ based solar cell can work well even at low temperature. Knowing the recombination rate and effective mobility in the thin film, the diffusion length is calculated to be $\sim 1 \mu\text{m}$ at room temperature. By monitoring the carrier density and diffusion length, we can measure perovskite performance.

Wehrenfennig *et al.* showed that MAPbI₃ exhibits long charge carrier diffusion lengths of $\sim 1 \mu\text{m}$ — a result of high charge-carrier mobility and low recombination rates, using TRTS and time-resolved photoluminescence (TRPL) [63]. Figure 3.14a presents excitation fluence-dependent transient THz signals $-\Delta E(t_{pp})/E(t_{pp})$ as a function of pump-probe time delay t_{pp} , where the transient signal $-\Delta E(t_{pp})/E(t_{pp})$

Figure 3.13: Obtained (a-b) carrier density and (c-d) mobility at (a, c) 18 K and (b, d) 285 K. Taken from Ref. [62]

is proportional to the photoinduced conductivity in material as described in Chapter 2. Using the rate equation to fit $-\Delta E(t_{pp})/E(t_{pp})$, they obtained recombination rate constants $\phi k_2 = 9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $\phi^2 k_3 = 4 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$ with ϕ being the photon-to-free-charge conversion ratio. Their first-order recombination rate constant ($k_1 = 2 \times 10^{-5} \text{ s}^{-1}$) was determined from TRPL at low pump fluence because of the long timescale (a few hundred nanoseconds). Figure 3.14b shows the first-, second-, third-order, and total recombination rate constants as a function of carrier density. As shown in Fig. 3.14b, first- and second-order recombination dominate when effective carrier density is between $10^{15} - 10^{17} \text{ cm}^{-3}$. With the ratio $\phi \leq 1$, the recombination rate constants (ϕk_2 and $\phi^2 k_3$, and total rate constant R_{total}) are the lower limits. The lower limit of carrier mobility $\phi\mu$ was obtained using Eq. 2.13. With R_{total} and $\phi\mu$, the lower limit of the diffusion length was calculated to be $\sim 1 \mu\text{m}$ using Eq. 2.14.

The knowledge of recombination kinetics enables TRTS to give guidance on

Figure 3.14: (a) Fluence-dependent frequency-integrated TRTS in MAPbI₃ and (b) extracted carrier decay rates. Taken from Ref. [63]

size-dependent physical properties. Motti *et al.* studied size-dependent samples of CsPbBr₃ using 1D TRTS. They compared the charge transport properties of bulk CsPbBr₃ and nanocrystal (NC) thin films (with NC size as 6, 7.5, and 10 nm) by using the recombination rate equation to fit the transient THz signal $-\Delta E(t_{pp})/E(t_{pp})$. The fits show that higher-order (second- and third-order) recombination dominates the carrier recombination processes. The obtained recombination rate constants increase with decreasing NC size which is attributed to the stronger overlap of electron and hole wave functions caused by the confinement effect [64]. The calculated effective mobility $\phi\mu$ decreases with increasing NC size, revealing the localized nature of the photogenerated carriers when CsPbBr₃ goes from bulk to quantum dots [65].

Besides TRTS, one can extract recombination rate constants from TA measurements. With the assumptions that (1) carrier distribution doesn't change and (2) the intrinsic bandgap varies slightly after photoexcitation, one can consider that the bleaching amplitude scales linearly with carrier concentration. Manser *et al.* studied the recombination mechanisms in MAPbI₃ thin film with TA, and found that the second-order mechanism is predominant as evidenced by striking linearity of $\Delta A^{-1}(\tau)$ (i.e., the inverse of bleaching amplitude) [66]. Fu *et al.* fitted the bleaching kinetics using Eq. 2.8, the extracted rate constants are consistent with literature values on MAPbI₃ ($k_1 = 2.3 \times 10^7 \text{ s}^{-1}$, $k_2 = 2.5 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$, $k_3 = 2.3 \times 10^7 \text{ cm}^{-29}\text{s}^{-1}$) [67]. The reported second-order rate constants in MAPbI₃ thin films using various techniques are on the order of 10^{-11} – $10^{-8} \text{ cm}^3\text{s}^{-1}$ [67–70]. Moreover, the

second-order rate constants in hybrid perovskites are as low as those found in single-crystalline inorganic semiconductors [71], and the second-order rate constants are several orders below the predicted value of Langevin's model [72]. Hence, one reason for high PCE in the perovskite solar cells could be a suppressed but predominant second-order recombination channel.

The TA spectra $[\Delta A(\hbar\omega, \tau)]$ gives the transient change in transitions corresponding to the probe energies. As described in Chapter 2, the phase-space filling effect (band filling effect) leads to a blueshift of the optical bandgap and a broadening of bleaching in TA spectra [66]. The phase-space filling induced blueshift of optical bandgap, which is called a dynamic Burstein-Moss shift [73, 74], is shown in Fig. 3.15c, and is carrier-density dependent with the expression

$$\Delta E_g^{BM} \propto N^{2/3}, \quad (3.3)$$

where ΔE_g^{BM} is the Burstein-Moss shift and N is the photogenerated carrier density. Manser *et al.* studied the Burstein-Moss dynamics in MAPbI₃ using TA [66]. They used the broadening in the normalized $\Delta A(\hbar\omega)$ to measure the Burstein-Moss shift of the optical bandgap (see Fig. 3.15a). Figure 3.15b shows the linear FWHM (full width at half maximum) dependence on $n_0^{2/3}$ which indicates that bandgap blueshift agrees well with the Burstein-Moss theory. One can use the FWHM of the normalized $\Delta A(\hbar\omega)$ to represent the Burstein-Moss shift only under the assumptions that (1) intrinsic bandgap varies only slightly (when the relation between FWHM and Burstein-Moss shift can then be established) and (2) excitonic contribution does not change with different injected carrier densities at the same pump-probe time delay (see details in Eq. 2.45, and Fig. 3.18). The linear curve presents an offset at a critical photogenerated carrier density $n_0 = 7.5 \times 10^{17} \text{ cm}^{-3}$. This critical carrier density can be used to characterize the emergence of the Burstein-Moss effect. With photogenerated carrier density larger than n_0 , bandgap shift due to the Burstein-Moss effect comes from occupied (unoccupied) states in conduction (valence) bands as shown in Fig. 3.15c.

Figure 3.15: Bandgap dynamics described by Burstein-Moss model. (a) Normalized $[\Delta A(\hbar\omega, \tau)]$ spectra with different injected photon density n_0 at 5 ps. (b) Bandgap as a function of n_0 . The curve shows offset at $n_0 = 7.5 \times 10^{17} \text{ cm}^{-3}$. (c) Illustration of modulation of band filling on bandgap. Taken from Ref. [66]

The TA spectra $[\Delta A(\hbar\omega, \tau)]$ can also show carrier cooling dynamics. Yang *et al.* reported carrier cooling after photoexcitation in MAPbI₃ as shown in Fig. 3.16. Figure 3.16a shows a typical pseudo-color plot of TA spectra. At short time delays after photoexcitation, the photogenerated carriers follow the Fermi-Dirac (FD) distribution. At the higher energy part of spectra, the FD distribution can be approximated by the Maxwell-Boltzmann (MB) distribution, yielding the expression

$$\Delta A(\hbar\omega) = -A_0 \exp\left(-\frac{\hbar\omega}{k_B T_e}\right), \quad (3.4)$$

where A_0 is a prefactor, T_e is the carrier temperature to characterize the kinetic energies of carriers, and k_B is the Boltzmann constant. The high-energy tail of the

normalized $[-\Delta A(\hbar\omega)]$ spectra can reflect the decreasing carrier temperature with increasing time delay (Fig. 3.16b), where the carrier temperature can be obtained using the MB equation to fit $-\Delta A(\hbar\omega)$. Figure 3.16c shows that higher pump photon energy generates carriers with higher excess energy. With 3.1-eV pump photon energy, the carrier cooling curve with high injected photon density (i.e. $6.0 \times 10^{18} \text{ cm}^{-3}$ in Fig. 3.16c) shows a slow carrier relaxation process. This slow carrier cooling phenomenon is caused by the presence of a hot phonon bottleneck, where photon emission and reabsorption by the carriers keep the carrier energy (and thus temperature) high. The slowing down of hot carrier cooling is one of the reasons for the excellent photovoltaic performance in lead halide perovskites [67, 75].

Figure 3.16: TA results on carrier cooling. (a) A typical pseudo-color plot of TA spectra of MAPbI₃. (b) Normalized $-\Delta A$ spectra between 0.1 ps and 3 ns. (c) Carrier temperature as a function of pump-probe time delay τ at different pump energy. (d) Carrier cooling curve with different input carrier density. Taken from Ref. [75]

3.2.4 Excitons in lead halide perovskites

Figure 3.17: Schematic illustration of (a) the free exciton and (b) the tightly bound exciton. Taken from Ref. [76]

In lead halide perovskites, the injected photon generates one electron in the conduction band, leaving one hole in the valence band. This pair of particles are created at the same point in space and can attract each other through the Coulomb interaction. When the interaction is large, this pair of charged particles forms an exciton. There are two basic types of excitons: (1) Wannier–Mott excitons, which are also called free excitons, are observed in semiconductors with a larger radius covering several unit cells. They can move freely in crystals. (2) Frenkel excitons, which are also called tightly bound excitons, often observed in insulators and molecular crystals. They have to move through crystal via hopping from sites to sites [76].

Lead-halide perovskites are reported to possess Wannier-type excitons with exciton binding energy E_b in MAPbI_3 ranging from 2 to 60 meV, that were measured with optical techniques that are sensitive to interband transitions near the exciton center-of-mass momentum $K \approx 0$ [77–81]. On the other hand, TRTS can detect intraband transitions across the entire K -space [82]. TRTS also has advantages in detecting intra-excitonic level transitions: those $1s$ - np (such as $2p$, $3p$, ...) transitions are the dominant transitions that occur in the THz range, so that one can calculate exciton binding energy E_b via excitonic transitions from the $1s$ ($E_b/1^2$) excitonic level to the

np states (E_b/n^2). Luo *et al.* reported contributions of intra-excitonic transition to the complex photoconductivity $\Delta\tilde{\sigma}$ using 2D TRTS and calculated exciton binding energy to be $E_b = 13.5$ meV. They claimed that their successful observation of intra-excitonic transitions arises from (1) the modification of the experimental setup using two 0.2-mm thick ZnTe for THz generation and detection, which increases the signal-to-noise ratio at the high-frequency region by an order of magnitude and (2) their choice of sample, where they used perovskite-poly(methylmethacrylate) (PMMA) thin film to increase the damage threshold of the perovskite material. Using resonant optical pulses to excite electrons from VBM to the $1s$ excitonic level, ground-state excitons can be generated. The THz pulses then excite these excitons from the ground state into higher excitonic levels. Figure 3.18b shows the real part of photoinduced THz response $\Delta\sigma_1$ and $\Delta\epsilon_1$ which are successfully fitted with combinations of two resonances and one broad Drude-Smith response. The two resonances correspond to transitions $1s \rightarrow 2p$ (≈ 10.1 meV) and $1s \rightarrow 3p$ (≈ 12.1 meV). The exciton dynamics are different under resonant and above bandgap excitations. While the buildup time is ~ 17 ps under resonant excitation (Fig. 3.18c), the buildup time under above bandgap excitation (3.1 eV, 399 nm) is much longer (10s of ps) as shown in Fig. 3.18. The much longer buildup time is attributed to the slow cooling process due to the hot-phonon effect [75, 82].

Compared to TRTS, TA spectra reflect interband transitions in the eV energy scale. TA spectra signals $[\Delta A(\hbar\omega, \tau)]$ arise from excitonic contribution (EC) and free carrier contribution (CC). Yang *et al.* successfully separated the EC and CC in their TA spectra with the help of absorption data taken at equilibrium [75]. The steady-state absorption spectrum is first disentangled into CC and EC. One then extracts the bandgap E_g , exciton binding energy E_b , and exciton bandwidth Γ from the fits (Fig. 3.19a). Taking into account the photoinduced changes in E_g , E_b , and Γ , the CC and EC to $\Delta A(\hbar\omega)$ are then separated as shown in Fig. 3.19b. Through fits to TA spectra, they extracted EC and CC at different injected photon density as shown in Fig. 3.19c. When the injected photon density is small, exciton quenching

Figure 3.18: (a) Illustration of TRTS: optical pump pulse is to excite 1s states; terahertz pulse is to probe intra-excitonic transitions. Sample is perovskite-PMMA thin film and the corresponding photoconductivity. (b) THz response functions at $T = 8\text{ K}$ and a pump-probe delay $t_{pp} = 60\text{ ps}$. The fits plotted in black solid line are combinations of Drude-Smith response and intra-excitonic transitions (1s $\rightarrow$ 2p in red dashed line and 1s $\rightarrow$ 3p in green dashed line). (c) Photoinduced change in conductivity $[\Delta\sigma_1(\omega)]$ at different τ with photoexcitation at (c) 790 nm and (d) 399 nm. Taken from Ref. [83]

dominates the bleaching effect, while with increasing n_0 , free carrier contribution induced bleaching begins to dominate [75]. Through the analysis, the corresponding time evolution of E_g , E_b , and Γ can be extracted, however, in Yang's work, only the values of 10 ps were given [75].

Figure 3.19: Excitonic and free carrier contributions to the steady-state $A(\hbar\omega)$ and $\Delta A(\hbar\omega)$. (a) Excitonic and free carrier contributions to steady-state A spectrum. (b) Injected photon density dependent TA data and fits at 10 ps. (c) Extracted CC and EC contribution as a function of n_0 . Taken from Ref. [75]

In the steady-state absorption spectra, the assumption of a parabolic band leads to a bad fit at the high energy tail [75]. Sestu *et al.* used a high-order coefficient R to account for the nonparabolicity in the band structure. The obtained fit matches data at the high energy part of absorbance spectra in MAPbBr₃. Their work thus enlarges the fitting range as shown in Fig. 3.20.

Figure 3.20: The steady-state absorption spectra fits with high-order coefficient R to account for the nonparabolic property in perovskites MAPbBr₃. Taken from Ref. [84]

3.2.5 Polarons in lead halide perovskites

When a carrier moves through the ionic lattice in lead-halide perovskites, the carrier will couple with the lattice, resulting in a quasiparticle called as polaron with a coupling constant

$$\alpha = \frac{1}{2} \frac{e^2}{\hbar} \sqrt{\frac{2m^*}{\hbar\omega_{LO}}} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right), \quad (3.5)$$

where $\hbar\omega_{LO}$ is the energy of a longitudinal optical (LO) phonon mode, m^* is the effective mass of the carrier, and ϵ_0 is the static dielectric constant, and ϵ_{∞} is the high-frequency dielectric constant [85].

Polarons in the perovskites are typically large polaron or Fröhlich-type polarons with the coupling constant $\alpha \approx 2$ [86,87]. When the spatial extent of the carrier is

less than a lattice constant, it is a small polaron. Small polarons can hop from one lattice site to another one at high temperature [88].

Time-resolved optical Kerr effect (TR-OKE) has been used to probe reorientation motions of molecular structures in liquids and solids by measuring the transient change in the birefringence induced by an applied electric field [89, 90]. After performing a fast Fourier transform (FFT) on the time domain data, phonon mode information at low frequencies ($<400\text{ cm}^{-1}$) can be extracted using this technique [91, 92].

In a crystalline solid, the TR-OKE transient is typically dominated by (1) instantaneous electronic and (2) ultrafast response, plus weak coherent oscillations attributed to Raman active phonon modes [93]. HOIPs are called crystalline liquids by Zhu *et al.* due to the coexistence of a crystalline-like response of charge carriers and a liquid-like response in the phonon response [94]. It is believed that HOIPs belong to the family of plastic crystals, with crystal structure possessing strong long-range translational order and local rotational disorder [94].

Polaron formation introduces a change in the electronic polarization, which can be detected by TR-OKE. Zhu *et al.* compared the TR-OKE responses in single-crystal CsPbBr_3 , MAPbBr_3 , and FAPbBr_3 [94]. The responses to the applied electric field of the three materials are different as shown in Fig. 3.21a–c. TR-OKE signals of CsPbBr_3 consist of contributions from (1) instantaneous electric response (gray area, due to pump–probe correlation) and (2) ultrafast response which is originated from inertial reorientation when there is polarization anisotropy [90, 95, 96]. The ultrafast response is contributed by local distortions of the unit cell i.e., PbBr_3^{-1} lattice [95]. On the other hand, signals from HOIPs have additional polarization relaxation regions as in molecular liquids: (3) subpicosecond component and (4) region between ~ 1 – ~ 2 ps component [89, 90]. The signals of HOIPs (Fig. 3.21b,c) in regions (3 and 4) are contributed by rotational motions and diffusive rotations of the molecular cations [97]. TR-OKE results reveal that molecular cations in HOIPs behave like molecular liquids which help to screen the carriers from interacting with

the environment while inorganic cations Cs^+ in CsPbBr_3 cannot [94]. Miyata *et al.* later performed TR-OKE experiments with a resonant and a nonresonant excitations on both of a single-crystal MAPbBr_3 and the all-inorganic perovskite CsPbBr_3 [95]. They claimed their TR-OKE results suggest polaron formation in both samples with subpicosecond timescale (0.3 ps for MAPbBr_3 , 0.7 ps for CsPbBr_3) contributed by PbBr_3^{-1} motions, resulting in charge carrier screening and low recombination rate in lead halide perovskites [94–96].

Figure 3.21: TR-OKE response of single-crystal all-inorganic perovskite (a) CsPbBr_3 and HOIP (b) MAPbBr_3 , and (c) FAPbBr_3 . Shaded area under gray dashed line denotes pump–probe cross correlation. Taken from Ref. [94]

We next explain why polaron formation can protect carriers from scattering and leading to a low recombination rate. In a polar semiconductor, the Coulomb potential V^{LR} is determined by

$$V^{LR}(\mathbf{r}) = - \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right] \frac{e^2}{|\mathbf{r}|}, \quad (3.6)$$

where $\mathbf{r}$ is the displacement between an electron and an ionic site. In lead halide

perovskites, ϵ_0 can be more than twice than the value of ϵ_∞ (e.g., MAPbI₃ shows high-frequency (optical) at ~ 5 and low-frequency (THz) at ~ 25) [98, 99], yielding a significant long-range Coulomb potential between the electron (or hole) and the ionic lattice, thus leading to large polaron formation [71]. Hence, in a deformable perovskite, upon photoexcitation, charge screening due to lattice deformation occurs [86]. The large polaron formation results in charge screening and reduced scattering with phonon modes, leading to slow hot carrier cooling and low second-order recombination rate [43, 71].

There are works done to claim the existence of polarons in perovskites using TRTS. Clinquanta *et al.* reported phonon mode frequency shift contributed by polaron formation from 2D TRTS data on CsPbBr₃ [100]. Normally, as absorption coefficient of perovskite in the THz region is small, a photoinduced phonon mode frequency shift is weak for thin-film perovskite. Clinquanta *et al.* measured a 3- μm thick CsPbBr₃ and obtained a strong peak shift of ~ 1.7 meV for the phonon mode at ~ 3.5 meV (~ 28 cm⁻¹). Note that for typical bulk CsPbBr₃, the THz absorption spectrum shows a broad peak centered around 2.3 THz [65]. What Clinquanta *et al.* used is CsPbBr₃ in low dimension [101] which I will describe in Chapter 6. Nevertheless, THz spectra analysis can reflect polaron dynamics.

TA is also a useful tool to measure polaron response. As described in Chapter 2, with a wide probe range, TA is able to detect the excited-state absorption which is the optical transition from the one excited state to the even higher excited state. Park *et al.* used transient excited-state absorption spectra to analyze polaron formation in MAPbI₃ perovskites with visible pump pulse (~ 560 nm) and probing in the near-infrared range (830–940 nm) as shown in Fig. 3.22b [102]. Their measurements were based on Frank-Condon excitation where both the electronic and the vibrational transitions can be excited, and then these vibrational states relax towards the polaronic state as shown in Fig. 3.22a. The residuals between exponential fits and data show oscillation features (Fig. 3.22c). After performing the FFT analysis, the obtained FFT spectra show expected oscillation modes at

~ 21 , ~ 44 , and ~ 74 cm^{-1} which are consistent with the results obtained from singular value decomposition. The DFT results predict the existence of the I–Pb–I bending modes (~ 21 cm^{-1} and ~ 45 cm^{-1}) and I–Pb–I c axis stretching mode at ~ 75 cm^{-1} [102]. The observed modes at ~ 110 and 150 cm^{-1} are likely due to MA's librational motion [102]. With weak intensity in the FFT spectra, MA reorientation motions are likely to be incoherent motions, while the principal modes (I–Pb–I bending and stretching modes) are coherent motions. After photoexcitation, the detected collective modes i.e., oscillations in TA kinetics correspond to the emerging polaronic states [102].

Figure 3.22: Transient excited-state absorption spectra of MAPbI₃. (a) Illustration of transient excited-state absorption with Frank–Condon excitations to push an electron from the ground state to the polaronic state. (b) A pseudo-color plot of transient excited-state absorption spectra. (c) The time profile measured at 840–855 nm. (d) FFT spectra measured in entire probe pulse range. (e) The FFT and LPSVD spectra are consistent. Taken from Ref. [102]

Lattice distance can be extracted from the low-energy-electron-diffraction (LEED) results. In a LEED instrument, electrons are first emitted from the cathode hitting the sample surface. Then the backscattered electrons are collected by a screen. The LEED patterns obtained from the measurements yield the distance between atoms on the surface. Chen *et al.* reported the LEED results of strontium titanate (SrTiO₃) at different oxygen vacancies. Surface reconstruction can be seen in the LEED patterns due to the alignment of oxygen vacancies. The LEED results can

infer polaron formation [103]. However, even the time-resolved LEED can only reflect the surface dynamics [104]. Photoinduced polaronic dynamics from TRTS and TA are still needed.

Low second-order recombination rates in perovskites are believed to be important reasons in why perovskites solar cells have high PCE. Both the ferroelectricity and polaron formation have been considered to be the reasons for the low recombination rates. Ferroelectricity in perovskites is still controversial. It is argued that the tetragonal phase of MPPbI_3 is centrosymmetric and should not display ferroelectricity [105]. However, theoretical studies through DFT calculations show a large electric polarization in MAPbI_3 [106]. Piezoresponse force microscopy (PFM) measurements on MAPbI_3 by different groups revealed the existence of ferroelectric/ferroelastic domains in HOIP that sustain long-lived hot carriers in HOIP [107,108]. Huang *et al.* attribute the confusing ferroic properties to the existence of both the nonpolar and polar regions co-existing in the material. Nonetheless, there is no strong evidence to support the existence of ferroelectricity, and the polar–nonpolar co-existence is consistent with the reported results up to now [109].

There were works trying to differentiate ferroelectricity and polaronic natures in the perovskites. Miyata *et al.* suggested a method to differentiate ferroelectricity and polaron formation via induced polarization change as shown in Fig. 3.23 [110]. Figure 3.23a shows the linear polarization response to an applied electric field in the conventional large polaron model. However, due to the disorder in lead halide HIOPs, their dielectric function is rather complex as shown in Fig. 3.23c, which leads to complex polarization responses (Fig. 3.23b). Comparable studies on polar liquid H_2O (Fig. 3.23d), ferroelectric material $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT, Fig. 3.23e), and the conventional semiconductor GaAs (Fig. 3.23f) reveal the typical dielectric functions $\tilde{\epsilon}$ [110]. Figure 3.23c and d show the similarity in $\tilde{\epsilon}$ in the gigahertz (GHz) region which arises from the reorientational relaxation of the polar molecule H_2O and organic cation MA^+ . Compared to $\tilde{\epsilon}$ of traditional semiconductor GaAs, $\tilde{\epsilon}$ of MAPbI_3 in the THz region is relative broader and complex which is similar

to ferroelectric properties in the ferroelectric material $\text{SrBi}_2\text{Ta}_2\text{O}_9$ as shown in Fig. 3.23e [110]. Hence, ferroelectricity and polaron formation should both contribute to the low recombination rate of lead halide HOIPs.

Figure 3.23: Ferroelectric and polaronic features in lead halide perovskites. Polarization responses of (a) Fröhlich large polaron and (b) Ferroelectric large polarons. Dielectric function (ϵ) of perovskite (c) MAPbI_3 (d) polar material H_2O (e) ferroelectric material $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and (f) conventional semiconductor GaAs . Blue (red) lines in (c–f) are real (imaginary) part of ϵ . Green line in c is corresponding phonon absorption spectrum. Taken from Ref. [110]

3.2.6 Interplay among free carriers, excitons and phonon modes

Among all the measurements to explore carrier and exciton dynamics, Zhao *et al.* performed a comprehensive study in elucidating the interplay among free carriers, excitons, and phonon modes using TRTS [86]. Zhao *et al.* performed TRTS measurements on the mixed-cation mixed halide perovskites $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$ thin film (FCPIB) [86]. The real part of complex conductivity $\sigma_1(\omega)$, as shown in Fig 3.24a, shows two low-lying phonon modes with energies at 0.85 THz ($\hbar\omega_{TO,1} = 3.6$ meV) and 1.80 THz ($\hbar\omega_{TO,2} = 7.4$ meV). Performing a loss function analysis, the corresponding LO phonon modes are found to be located at 1.15 THz ($\hbar\omega_{LO,1} =$

Figure 3.24: THz transmission signals in time domain passing through FCPiB sample (blue solid line) and reference crystal (yellow solid line) at 15 K with an excitation photon energy of ~ 1.57 eV. Purple dashed line is transient change in THz electric field. (b) The real part of complex conductivity in equilibrium is shown in yellow dashed line. Transient change in the THz conductivity (purple circle line) is obtained with the subtraction of $\Delta\sigma_1(\omega)$ at τ from $\Delta\sigma_1(\omega)$ at equilibrium. The real (c) and imaginary (d) parts of complex photoconductivity spectra at certain pump-probe time delays at 15 K. Circle lines denote data while dashed lines are to represent model fits. The model considers contributions from peak shift in phonon (yellow shaded area) and carriers in disordered system (purple shaded area). Taken from Ref. [86]

4.8 meV) and 3.57 THz ($\hbar\omega_{LO,2} = 14.8$ meV). Figure 3.24c and d show the extracted photoinduced change in complex conductivity $\{[\Delta\sigma_1(\omega)], [\Delta\sigma_2(\omega)]\}$. The transient

conductivity can be fitted successfully with a combination of the expressions of the Drude-Smith model and a peak-shift model. The peak-shift model is to describe the frequency shifts and changes in amplitudes of the phonon modes, and it is the first-order differential to the Lorentz model arising from phonon anharmonicity [86]. From the Drude-Smith contribution, one can extract charge carrier density (via Drude plasma frequency) and carrier scattering rate (via Drude scattering rate). From the change in Lorentzian spectral weight, change in phonon frequency, and the static Lorentz parameters).

Figure 3.25: Illustration of energy-dependent carrier relaxation channels and carrier scattering rate dynamics. (a) Optical excitation generates free carriers with excess energy covering regions i, ii, iii which can be determined by phonon modes energies. (b) Regions i,ii,iii are corresponding to 4,3,2 scattering channels, respectively. (c) The calculated state occupancy from the Fermi-Dirac distribution at different temperatures. (d) the extracted carrier scattering rate shows step like transitions. (e) At 65 K, the scattering rate is close to 2. While at 285 K, the scattering rate is at a slightly higher value. Taken from Ref. [86]

With near bandedge excitation, photogenerated carriers can relax down toward to CBM with excess energy above the two lowest-lying phonon modes 3.25a). The three regions determined by $\hbar\omega_{LO,1}$ and $\hbar\omega_{LO,2}$ are shown in Fig. 3.25a. In region i where excess energy $E > \hbar\omega_{LO,2} > \hbar\omega_{LO,1}$, the phonon modes $\hbar\omega_{LO,2}$ and $\hbar\omega_{LO,1}$ can both be absorbed and emitted, so there are four scattering channels (SCs). In region

Figure 3.26: (a) Inverse of n^2 is linear to pump-probe delay τ , which indicates third-order recombination dominates. (b) Evolution of carrier density n (c) Peak shift in spectral weight. (d) Illustration of interplay among carriers, phonon modes and excitons. Taken from Ref. [86]

ii where $\hbar\omega_{LO,2} > E > \hbar\omega_{LO,1}$, three SCs are allowed with two phonon absorption SCs and one phonon emission SC. In region iii, the carrier excess energy is not enough to emit phonons with energy $\hbar\omega_{LO,2}$ and $\hbar\omega_{LO,1}$, hence, only two SCs (absorption of the two phonon modes) can exist. Considering the state occupancy difference at different electronic temperatures (Fig. 3.25c), in equilibrium, four SCs exist at room temperature, while only two SCs open up at 15 K. Thereafter at 15 K, at short time delays, the scattering rate undergoes almost step-like SCs transitions: 4 SCs $\rightarrow$ 2 SCs $\rightarrow$ 1 SC. The SC transition rises from photocarriers relaxing from region i down towards region iii at 15 K. As a comparison, at 65 and 285 K, scattering rates are

consistent with ~ 2 SCs because of the larger thermal energy.

A graph of $1/n^2$ versus pump–probe time delay is linear between 10 and 600 ps indicating that third-order recombination is predominant. After subtracting the third-order recombination curve from the experimental carrier density, we obtain the purple shaded area in Fig. 3.26b. It shows that at short time delays, the carrier density decreases, followed by an increase at ~ 2 ps (Fig. 3.26b). Taking into account the corresponding change in phonon spectral weight (Fig. 3.26c), we see the increase in the carrier density corresponds to a decrease in the spectra weight of both phonon mode 1 and 2 in the green shaded area. As a result, Zhao *et al.* proposed the mechanisms after photoexcitation: (1) carrier experience relaxation and third-order recombination; (2) relaxation of carriers with phonon emission; (3) exciton formation with concomitant decreasing carrier density; (4) exciton dissociation into carriers via phonon absorption which can in turn increase carrier density. This complicated interplay among free carriers, phonons, and excitons leads to the presence of long-lived free carriers in the mixed-cation mixed-halide perovskites. Their work illustrates the power of TRTS in characterizing solar cell materials.

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Chapter 4

Exploring the role of stoichiometry in the photovoltaic performance of $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 1$ and 1.2) thin films using time-resolved terahertz spectroscopy

*In this chapter, a systematic study of all-inorganic perovskite $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 1$ and 1.2) thin film samples using TRTS was performed. By modeling photoinduced change in optical conductivity with the Drude-Smith model, the charge carrier density and effective mobility were extracted. TRTS results showed, compared to conventional stoichiometric perovskite CsPbI_2Br thin film, overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ alloy can generate more free carriers and possess a higher photon-to-charge quantum yield at short time delays upon photoexcitation. This work has been published in *J.Mater.Chem.C* 2019,7,5314–5323.*

4.1 Introduction

With the evolution of lead halide perovskite solar cells, there is general consensus that instability issues in lead halide perovskites limit their photovoltaic performance [1]. Instability issues in lead halide perovskites arise from sensitivity in perovskites towards (1) water and moisture [2, 3], (2) light and oxygen [4, 5], (3) thermal stress [6, 7] and (4) electric field during the operation of photovoltaic devices, resulting in degradation of perovskite solar cells [8, 9]. There are several methods to enhance perovskite stability and hence boost perovskite solar cell performance including: (1) mixing HOIP and/or all-inorganic perovskites [10, 11], (2) adding additives to stabilize the perovskite system [12, 13], and (3) replacing organic cations with all-inorganic cations [14]. A PCE of 22.1% in a single-junction perovskite solar cell system based on the mixed-cation perovskite $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ was reported by Yang and his coworkers [15]. The highest certified PCE of 25.2% was achieved by KRICT/MIT team using a quadruple-cation perovskite as light absorber [11, 16]. The PCE of all-inorganic perovskite solar cells reaching $\sim 17\%$ was reported using Rb-incorporated CsPbI_2Br [14]. So far, only $\sim 84\%$ of the Shockley–Queisser (SQ) efficiency limit has been obtained using single-junction organometal lead-halide perovskite solar cells, while for all-inorganic lead halide perovskites, only $\sim 71\%$ of the SQ efficiency limit has been obtained [17, 18]. Therefore, there is still room in all-inorganic perovskite solar cells to reach the PCE SQ limit. Moreover, Kulbak *et al.* showed that all-inorganic perovskite-based cells can work equally well with HOIPs in terms of the value of their open-circuit voltage [19]. Hence, the further exploring of all-inorganic perovskite cells is desirable.

According to the SQ efficiency limit, the PCEs of perovskites can reach their highest value with a bandgap around $E_g \sim 1.38$ eV [17, 20]. Conventional all-inorganic CsPbI_3 has a suitable bandgap (~ 1.73 eV) but suffer from thermal instability at room temperature, i.e., the perovskite phase (black α -phase) degrades into a non-perovskite phase (yellow δ -phase) [12]. This thermal instability in CsPbI_3 is due to the size of Cs^+ ion being too small to stabilize the perovskite lattice in

the presence of the I anions [21, 22]. On the other hand, all-inorganic perovskite CsPbBr_3 possesses robust thermal stability; but a relatively low PCE because of its large bandgap (~ 2.3 eV), which can be explained by the relation between the SQ limit and bandgap [19, 23]. Balancing between low bandgap and high thermal stability in the $\text{CsPbI}_{3-x}\text{Br}_x$ ($x = 0, 1, 2, 3$) series, CsPbI_2Br (i.e. $x = 1$) perovskites have attracted intense attention [24, 25]. However, the bandgap of CsPbI_2Br (~ 1.9 eV) is still larger than the optimum value [24]. To find the right balance between stability and photovoltaic performance, the effect of stoichiometry on photovoltaic performance and film stability has been investigated. Ma *et al.* compared three kinds of perovskite systems: (1) CsBr-rich CsPbI_2Br , (2) stoichiometric CsPbI_2Br , and (3) PbI_2 -rich CsPbI_2Br , and found that CsBr-rich CsPbI_2Br films show the best stability upon air exposure while the stoichiometric CsPbI_2Br films give the best photovoltaic performance [26]. The CsBr-rich $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.6}$ was obtained from blending an overstoichiometric amount of CsBr with PbI_2 .

To assess how the phase stabilities of all-inorganic perovskite CsPbI_2Br and their overstoichiometric derivatives are related to the realistic solar cell performance, our coworkers performed a systematic study on the optical and structural properties of all-inorganic perovskites $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 0.95\text{--}4$) and their respective solar cell device performance (e.g., PCE and current density) [27]. Figure 4.1a shows the evolution of absorption spectra of all-inorganic perovskite $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 0.95\text{--}4$) thin films with different chemical composition x . The black line in Fig. 4.1a is the absorption spectrum of stoichiometric CsPbI_2Br with the bandgap at ~ 620 nm and a shoulder between ~ 400 nm and ~ 450 nm. Increasing amounts of CsBr (i.e. increasing x) results in the bleaching of the absorption bands at 400–650 nm which are characteristic for CsPbI_2Br in the cubic phase. It is interesting to see that, for $x < 1.5$, the absorption spectra show similar profiles. The peak that appeared from 380–405 nm corresponds to mixed-halide Cs_4PbX_6 ($X = \text{I}, \text{Br}$) [28]. X-ray powder diffraction (XRD) patterns (4.1b) shows the existence of highly crystalline cubic CsPbI_2Br and rhombohedral I-rich Cs_4PbX_6 ($X = \text{I}, \text{Br}$) in the alloys with $1 < x <$

1.5 compositions. The XRD pattern of overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ (Fig. 4.1) can prove the cubic CsPbI_2Br features in the material, and the absorption spectrum of the overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ shows a similar profile as the stoichiometric CsPbI_2Br thin film.

Figure 4.1: Systematic studies on all-inorganic perovskites $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 0.95$ –4) using (a) steady-state absorption spectroscopy and (b) XRD. XRD patterns of rhombohedral phase of Cs_4PbX_6 , orthorhombic (Olive green square) and cubic (light blue square) phases of CsPbI_2Br are shown, respectively. One can recognize cubic CsPbI_2Br from the XRD patterns at $2\theta = 14.7, 20.9, 29.7, 33.6,$ and 37.8 . With $x < 1.05$, features of orthorhombic and cubic phases of CsPbI_2Br are obvious. While with $x > 1.05$, the features of orthorhombic CsPbI_2Br are gradually eliminated with emerging features of Cs_4PbX_6 denoted with red and blue stars ($X = \text{I, Br}$). Taken from Ref. [27]

The overstoichiometric $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 1.2$ –1.5) can maintain its phase within 300 hours [27]. Figure 4.2b shows the stable absorption spectra of $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ with time. Meanwhile, stoichiometric CsPbI_2Br degrades completely into CsPbI_3 and CsPbBr_3 under the same condition as shown in Fig. 4.2a. The corresponding XRD patterns (Fig. 4.2c) prove the degradation in stoichiometric CsPbI_2Br into orthorhombic δ - CsPbI_3 and cubic α - CsPbBr_3 , while the overstoichiometric sample maintain the phase cubic α - CsPbBr_3 for as long as 1000 h (Fig. 4.2d).

Figure 4.3 shows that the additional CsBr in the stoichiometric CsPbI_2Br thin film can enhance the PCE of the corresponding solar cell system. The enhancement is highest with composition $x = 1.2$ ($\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$). Compared to stoichiometric CsPbI_2Br , overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ shows (1) fairly stable and (2) better

Figure 4.2: Long-term stability in the stoichiometric (CsPbI_2Br) and overstoichiometric ($\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$) all-inorganic perovskites using absorption spectrometry (a and b) and XRD (c and d). Taken from Ref. [27]

photovoltaic performance with PCE exceeding 10% as compared to conventional CsPbI_2Br (with a PCE as 6.9% under same operation conditions) as shown in Fig. 4.3. The formation of the Cs_4PbX_6 impurity phase correlates with the improved morphology and crystallinity of the overstoichiometric material as compared to the conventional CsPbI_2Br [27], leading to a better photovoltaic performance in this material.

TRTS technique is a powerful tool to study the intrinsic transport properties that are important in device applications, such as carrier density, carrier mobility, diffusion length, and quantum yield upon photoexcitation. With the help of TRTS technique, Yettapu *et al.* studied intrinsic transport properties of colloidal CsPbBr_3 perovskite nanocrystals [29]. They found that those nanocrystals possess high carrier mobility ($\sim 4500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), long diffusion length ($> 9.2 \mu\text{m}$), and high

Figure 4.3: Best and averaged PCEs in solar cells using all-inorganic perovskites $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 0.95\text{--}4$). Taken from Ref. [27]

luminescence quantum yield (80%) which make those materials good light-emitting devices [29]. To explore the physics behind the better photovoltaic performance of the overstoichiometric perovskite $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$, TRTS measurements on CsPbI_2Br and $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ were performed. The samples were grown by Frolova *et al.* from Prof. Pavel Troshin's group (Skolkovo Institute of Science and Technology) [27]. Precursor cesium bromide (CsBr , 99.9% from Aldrich) and lead (II) iodide (PbI_2 , 99.9% from Aldrich) were thermally coevaporated in a vacuum chamber integrated inside an MBraun glove box at the balanced deposition rates of $0.5\text{--}2 \text{ \AA}$. Sequential layer-by-layer deposition of CsBr and PbI_2 produced perovskite thin films with different compositions, i.e. $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 1$ and 1.2) [27]. Both samples were pumped with 400-nm laser pulses, at a fluence of $16.6 \mu\text{J}/\text{cm}^2$ at 285 K, and probed with THz pulses at a series of well defined pump-probe delays (t_{pp}).

4.2 Results and discussion

4.2.1 1D TRTS results

In TRTS, the zero pump-probe delay is defined using 1D TRTS, when the photoinduced change of the transmitted THz electric field, $-\Delta E$, starts to deviate from zero. Figure 4.4 shows, for the overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ thin film sample, a sharp decay process in $-\Delta E(t_{pp})/E(t_{pp})$ (t_{pp} is the pump-probe time delay). On the other hand, for the stoichiometric thin film sample, $-\Delta E(t_{pp})/E(t_{pp})$ curve (yellow) does not decay, showing a long-term process beyond our detection time window. Both samples show similar $-\Delta E(t_{pp})/E(t_{pp})$ values at ns scales, suggesting the overstoichiometric sample show an additional sharp decay process on top of a slow decay process as that in the stoichiometric sample. The additional sharp decay process, indicating more photogenerated carriers, suggests a better photovoltaic performance of the overstoichiometric thin film sample. However, due to the lack of frequency resolution in 1D TRTS, $-\Delta E(t_{pp})/E(t_{pp})$ curve represents the decay of the product of charge carrier numbers N and carrier mobility μ , i.e. $N\mu$. To further extract carrier density dynamics and the evolution of carrier mobility, frequency-resolved (i.e. 2D) TRTS was employed.

4.2.2 2D TRTS results

To perform frequency-resolved TRTS, a z -cut quartz crystal is used as a reference. Both the overstoichiometric and stoichiometric $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 1$ and 1.2) thin films are deposited onto z -cut quartz substrates. According to the analysis procedures described in Chapter 2, to extract photoinduced change from the sample, we adopted $n = 2.1118 - 0.004f + 0.0028f^2$ and $k = 0.00146 - 0.0007f + 0.0001f^2$ (f is frequency) for the refractive index of z -cut quartz substrate [30]. Hence, static and photoconductivity from $\text{Cs}_x\text{PbI}_2\text{Br}_x$ ($x = 1, 1.2$) thin films can be extracted via TRTS analysis procedures described in Chapter 2. The extracted photoinduced

Figure 4.4: Frequency-integrated TRTS results of overstoichiometric (blue dots) $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ and stoichiometric (orange dots) CsPbI_2Br thin films. Respective exponential fits are plotted in blue and orange solid lines. The inset figure show the 1D TRTS data between -10 ps and 100 ps.

change in THz complex conductivity $\Delta\tilde{\sigma}_{t_{pp}}$ has the expression

$$\Delta\tilde{\sigma}_{t_{pp}}(\omega) = \tilde{\sigma}_{t_{pp}}(\omega) - \tilde{\sigma}_{-5 \text{ ps}}(\omega). \quad (4.1)$$

The complex optical conductivity spectra at -5 ps are chosen as the response at equilibrium, as indicated in the inset figure in Fig. 4.4. Figure 4.5 shows the extracted real and imaginary parts of photoconductivity at certain time delays for both samples (Fig. 4.5a-b for $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ and Fig. 4.5c-d for CsPbI_2Br). The wiggles in $\Delta\tilde{\sigma}_{t_{pp}}(\omega)$ arise from the low signal-to-noise and electronic noise from the setup.

Both samples show a nearly flat $\Delta\sigma_{2,t_{pp}}(\omega)$ and a peak at finite frequency in $\Delta\sigma_{1,t_{pp}}(\omega)$ indicating a Drude-Smith response in $\Delta\tilde{\sigma}_{t_{pp}}(\omega)$. The Drude-Smith response has been reported on various heavily disordered halide perovskites [31, 32]. The Drude-Smith model in photoconductivity has a Drude term $\tilde{\sigma}_D(\omega)$ and a Smith

Figure 4.5: (a, c) The Real ($\Delta\sigma_{1,t_{pp}}$) and (b, d) the imaginary ($\Delta\sigma_{2,t_{pp}}$) parts of photoconductivity of (a-b) the overstoichiometric and (c-d) the stoichiometric CsPbI₂Br thin films at 5 ps (red dot lines), 10 ps (blue dot lines), 20 ps (yellow dot lines), and 60 ps (green dot lines). Corresponding fits are plotted in solid lines.

term $\tilde{\sigma}_S(\omega)$ as described in Eq. 2.28. Solid lines in Fig. 4.5 are the Drude-Smith fits to $\Delta\tilde{\sigma}_{t_{pp}}(\omega)$.

From the Drude-Smith fits, fitting parameters (1) the plasma frequency $\omega_p(t_{pp})$ and (2) the scattering rate $\gamma(t_{pp})$ at pump-probe time delays t_{pp} can be extracted, resulting in the extraction of carrier density $N(t_{pp})$ via

$$N(t_{pp}) = \omega_p^2(t_{pp})\epsilon_0 m^*/e^2, \quad (4.2)$$

where e is the elementary charge of carriers and m^* is the electron-hole reduced mass ($m^* = 0.12 m_0$) [29]]. The effective mobility μ_{eff} in the Drude-Smith model can be extracted via Eq. 2.31. Figure 4.6 shows the extracted carrier density and effective mobility for both samples.

Figure 4.6a shows that Cs_{1.2}PbI₂Br_{1.2} has a larger photogenerated carrier density than the CsPbI₂Br at short time delays. To compare the photovoltaic performance

Figure 4.6: Carrier densities and effective mobilities of (a) the overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ and (b) the stoichiometric CsPbI_2Br thin films. Taken from Ref. [27]

between the two samples, we define the photon-to-charge quantum yield as $\phi = n_0/n_{ph}$, where n_0 is the initial photogenerated carrier density and n_{ph} is the absorbed photon density. Considering the very similar absorbance of both samples at 400 nm as shown in Fig. 4.1a-b, the larger carrier density in the $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ sample at short time delays implies a higher quantum yield in this material. Moreover, the extracted mobility dynamics (Fig. 4.6b) shows that both samples have a similar mobility of $\sim 600 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. As the current density j is proportional to the product of carrier density $N(t_{pp})$ and carrier mobility μ_{eff} via $j \propto \mu_{eff}n$, our extracted $N(t_{pp})$ and $\mu_{eff}(t_{pp})$ show that at short time delays, the current density is larger for the $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ sample as compared to CsPbI_2Br . As a result, our TRTS results suggest a better photovoltaic performance in this overstoichiometric sample compared to the stoichiometric sample.

In the case of $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ thin film, the inverse of carrier density ($1/N(t_{pp})$) is linear in t_{pp} , suggesting that recombination is predominantly second-order with the second-order rate constant $k_2 = 1.33 \times 10^{-7} \text{ cm}^3\text{s}^{-1}$ and the initial carrier density $N_0 = 5.4 \times 10^{16} \text{ cm}^{-3}$ from fits to rate equation (Eq. 2.10) as shown in Fig. 4.7a. The initial carrier density N_0 is an extracted carrier density at time zero. Our extracted carrier recombination rate k_2 is larger than the published ones that are on

Figure 4.7: (a) The inverse of carrier density curve $N^{-1}(t_{pp})$ in black squares indicates a second-order carrier recombination process. The red solid line in (a) is the linear fit to the $N^{-1}(t_{pp})$ (b) Carrier recombination rate equation fitting curve [red solid line in (b)] to $N(t_{pp})$ (black triangles) implies a second-order recombination process.

the order of 10^{-11} – 10^{-8} cm^3s^{-1} using various techniques including TRTS [31,33–36]. The larger recombination rate indicates the PCE of the overstoichiometric material could be pushed up more. Using the parameters obtained from the fits, the carrier density N is plotted in red solid line in Fig. 4.7b, which fits the experimental N well (black triangles in Fig. 4.7b).

4.3 Conclusion

In conclusion, as compared to conventional CsPbI_2Br , the overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ alloys show improved film morphology, improved thermal and photochemical stabilities, superior electronic and photovoltaic properties in both thin film samples and photovoltaic cells. Our TRTS results reveal the underlying physics behind the better photovoltaic performance overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$: (1) a larger carrier density than that of CsPbI_2Br , (2) a similar mobility as CsPbI_2Br , and (3) a higher quantum yield at short time delays than that of CsPbI_2Br .

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Chapter 5

Carrier and exciton dynamics in mixed-cation lead mixed-halide perovskite thin films

Compared to all-inorganic perovskites and hybrid organic-inorganic perovskites, mixed-cation lead mixed-halide perovskites like $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$ (FCPIB) can simultaneously achieve high power conversion efficiency and structural stability. A thorough understanding of the photophysical properties underpinning the superior photovoltaic performance is needed. In this chapter, we performed transient absorption (TA) measurements on FCPIB samples with above-bandgap and bandgap pump photons. We fitted the TA data taking into account the nonparabolic nature of the valence band and the conduction band, and found a positive bandgap renormalization (BGR) which disagrees with previously the reported negative BGR values in other members of the halide perovskite family. Consistent to previous reports, we observed slow hot-carrier cooling with above-bandgap pump at high fluences. We successfully extracted the time evolution of photogenerated electron density and exciton oscillator strength, which has not been reported before. The obtained exciton oscillator strength reveals a photoinduced exciton formation, which could play a role in the long carrier lifetime in the perovskites.

5.1 Introduction

Lead halide perovskites exhibit properties of large absorption coefficients [1,2], long and balanced electron and hole diffusion lengths [3], and low excitation threshold of hot-carrier cooling due to hot-phonon bottleneck [4], that makes them excellent solar cell materials. This family of perovskites has been extensively studied in the field of photovoltaic [5–10], LEDs [11,12], and lasing [13,14]. Single-junction perovskite solar cells (PSCs) based on a quadruple-cation perovskite system exhibit world-record PCE of up to 25.2% [15,16]. At the present time, the mixed-halide perovskites can easily deliver high PCE over 20% and long-term stability against degradation by light, water, or air [17–20], e.g., mixed-cation lead mixed-halide perovskites exhibit both high-efficiency PCEs of 22.1% and long-term stability [21].

Simulations of free charge fraction over the total excitation density by D’Innocenzo *et al.* showed that, under photovoltaic cell operating conditions (e.g. at room temperature and low excitation density), the fraction is approaching one, i.e. the photogenerated excitons are fully ionized into free carriers, while the fraction decreases with increasing excitation density, indicating increasing amounts of exciton populations [40]. Note that upon photoexcitation, the distribution of free carriers and excitons strongly depends on pump fluence. Therefore, both free carrier and exciton dynamics under various pump fluences must be taken into account while analyzing the data.

A previous TRTS work reported the unique interplay among free carriers, excitons, and phonons in a mixed-cation and mixed-halide perovskite $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$ (FCPIB) [25]. Terahertz photons possess meV energy, therefore TRTS is sensitive to intra-excitonic level transitions. In contrast, TA uses photons with enough energy to overcome the near-infrared bandgap, to probe the transient responses involving the conduction band, valence band, and excitonic levels.

Pioneer TA works [4, 22, 26, 27] have uncovered key parameters, such as carrier temperature and the transient change in the bandgap, assuming the Fermi-Dirac

(FD) distribution of the carriers and the parabolic band near the band edges. However, in these reports, the time evolution of the carrier density or exciton contribution has not been resolved. A proper analysis of TA spectra should yield carrier and exciton dynamics all within one self-consistent picture. In our work, we disentangle the exciton contributions from the free carriers by using a broadband white-light probe (1.5–2.0 eV), which then tells us the roles that excitons and carriers play in the photovoltaic properties of these FA-based perovskite materials.

5.2 Results and Discussion

FA_{0.85}Cs_{0.15}Pb(I_{0.97}Br_{0.03})₃ thin film was grown by Dr. Chen Bingbing from Professor Lam Yeng Ming’s group (MSE, NTU). The perovskite precursor solution was prepared by dissolving the precursors FAI, CsI, PbI₂, and PbBr₂ with respective stoichiometric ratio in a mixed organic solvent system comprising anhydrous N,N-dimethylformamide (DMF) and anhydrous dimethyl sulfoxide (DMSO) at the volume ratio of DMF:DMSO = 4:1. The *z*-cut substrate was cleaned with Hellmanex II solution (1% v/v), deionized water, acetone, and isopropyl alcohol in an ultrasonic bath for 15 min, and then treated with an air plasma treatment for 15 min and subsequently transferred to a nitrogen glove box for the deposition of perovskite films. The perovskite film was prepared by spin-coating the perovskite solution (0.5 mol/L) on quartz substrate at 1000 r.p.m. for the first 10 s and 4000 r.p.m. for the following 30 s. Chlorobenzene (200 μ L) was dripped fast on the sample surface at 15 s before finishing the spin-coating. Immediately, the substrate was placed on a hotplate for thermal annealing at 80°C for 5 min, then 120°C for 5 min, and then 180°C for 30 min.

5.2.1 Steady-state absorption spectra

The steady-state absorption spectra measurement was performed by our collaborator Ms. Chen Xiaoxuan from Professor Sun Handong’s group using variable angle

spectroscopic ellipsometry (VASE) in the transmission mode. The film sample was illuminated by a halogen lamp and the transmitted light was then resolved by a monochromator and collected by a photomultiplier.

The obtained steady-state absorbance spectra (Fig. 5.2a) exhibit an absorption onset at ~ 1.6 eV and a monotonic increase with photon energy. These features agree with reports on the same compound [25] and their relatives (MAPbI₃) [28]. Yang *et al.* employed a detailed model, based on Elliott's theory [29], to analyze both the steady-state and transient absorption spectra, assuming both the conduction band and valence band possess parabolic dispersion [4, 30]. Thereafter, many works follow this same parabolic-band assumption in their fits to steady-state absorption, and subsequent transient absorption data analysis [26, 27].

Accurate fits to steady-state absorption spectra are crucial in analyzing subsequent transient absorption data, since the extracted fitting parameters are fixed in fitting $\Delta A(\hbar\omega)$. We follow Elliott's very original formula [29, 31]. In addition, Saba *et al.* [32, 33] revealed that the steady-state absorption spectra should be fitted by introducing a nonparabolic factor, especially for photon energies well above the bandgap. We follow their method to perform a nonlinear least-squares fitting routine, using $A(\hbar\omega) = A_{CC}(\hbar\omega) + A_{EC}(\hbar\omega)$, where the carrier contribution (CC) term is

$$A_{CC}(\hbar\omega) \propto \mu_{cv}^2 \frac{2\pi\sqrt{E_b}}{\hbar\omega} \frac{1}{\Gamma} \int_{E_g}^{\infty} \text{sech}\left(\frac{\hbar\omega - E}{\Gamma}\right) \frac{\xi(E - E_g)}{1 - \exp(-2\pi\sqrt{\frac{E_b}{E - E_g}})} dE, \quad (5.1)$$

and the exciton contribution (EC) term is

$$A_{EC}(\hbar\omega) \propto \mu_{cv}^2 \frac{2\pi E_b^{3/2}}{\hbar\omega} \frac{1}{\Gamma} \sum_{j=1}^7 \frac{1}{j^3} \text{sech}\left(\frac{\hbar\omega - E_g + E_b/j^2}{\Gamma}\right), \quad (5.2)$$

where μ_{cv}^2 is the transition dipole moment, E_g is the bandgap, E_b is the exciton binding energy, $(E_g - E_b/j^2)$ is the energy of the j^{th} excitonic state, the $E_b^{3/2}$ in the EC term arises from the coupling between the wavefunctions of an electron and a hole [34], Γ is the exciton bandwidth and $\xi(E - E_g) = 1 + 10R(E - E_g) + 126R^2(E - E_g)^2$ is

Figure 5.1: Steady-state absorption spectrum fits using the fitting equation without the nonparabolic factor R with different fitting ranges: (a) 1.5–2 eV, (b) 1.5–1.9 eV, and (c) 1.5–1.8 eV.

to account for band nonparabolicity effect with R being the nonparabolic factor [33].

Here we follow Sestu *et al.* by employing the hyperbolic secant functions in the convolutions to account for the finite linewidth Γ . In the EC term, the $\frac{1}{\Gamma}$ factor is to normalize the amplitude induced by hyperbolic secant functions. The EC term is a measure of the excitonic oscillator strength. Using this nonparabolic term enables us to fit the data over a wide range of photon energies (see Fig. 5.1 and Fig. 5.2). Figure 5.1 shows that, without the nonparabolic term R , when we change the fitting range from 1.5–1.8 eV to 1.5–2 eV, the fitting quality became bad. Table 5.1 show the extracted E_b and E_g with large error bars, without R included in the fitting model. Once we include the effect of nonparabolicity, we can fit the steady-state absorption spectra from 1.5 eV to 2 eV as shown in Fig. 5.2. Through this absorption spectra analysis, we conclude that, if we include the R terms in the fitting model, not only the fitting quality is better, the fitting energy range is also larger. Also, compared to the obtained fitting parameters without R as shown in Table 5.1, we find that the obtained fitting parameters (Table 5.2) are relatively stable when we change the fitting ranges when we include R in the fitting model.

Table 5.1: Fitting parameter of linear absorption spectroscopy without R included

Obtained fitting parameter		
Fitting range	E_b (meV)	E_g (eV)
1.5–2 eV	0.02 ± 0.01	1.645 ± 0.010
1.5–1.9 eV	0.02 ± 0.03	1.625 ± 0.002
1.5–1.8 eV	2.5 ± 0.3	1.608 ± 0.002

Figure 5.2: Steady-state absorption spectra fits using the fitting equation with R included in the ξ term with different fitting ranges: (a) 1.5–2 eV, (b) 1.5–1.9 eV, and (c) 1.46–1.8 eV. When the fitting range is up to 1.8 eV, due to the fluctuation at ~ 1.5 eV, we can not fit from 1.5 eV, and need to fit from at least ~ 1.46 eV.

Table 5.2: Fitting parameter of linear absorption spectroscopy with R included

Obtained fitting parameter		
Fitting range	$E_b(\text{meV})$	$E_g(\text{eV})$
1.5–2 eV	26.1 ± 6.3	1.638 ± 0.009
1.5–1.9 eV	19.3 ± 5.5	1.625 ± 0.007
1.46–1.8 eV	13.6 ± 0.8	1.594 ± 0.001

For the spectra near the bandedge, both fitting models with or without the nonparabolic term yield qualitatively same fits (See Fig. 5.1c and Fig. 5.2a). A fit to the data, shown in Fig. 5.2a, yields $E_g = 1.636 \pm 0.008$ eV and $E_b = 25 \pm 6$ meV. We then fix these extracted parameters in the fitting model to fit the subsequent transient absorption data.

5.2.2 Determination of carrier temperature

Next we measured the transient absorption spectra on FCPIB with above-bandgap (400 nm) and bandgap (or resonant) 770-nm excitations. Figure 5.3a shows the normalized TA spectra $-\Delta A(\hbar\omega)$ at representative time delays from 0.5 ps to 1 ns under 400-nm pump with a fluence of $83 \mu\text{J}/\text{cm}^2$. A photoinduced absorption (PIA) observed below the bandgap at short time delays (e.g. 0.5 ps) has been attributed to the presence of additional optical transitions due to bandgap renormalization (BGR), rather than biexciton formation [35]. A large bleaching feature at energies above the bandgap implies excited states occupied by photogenerated carriers and excitons. The probe photon energy dependence of the bleaching yields a photo

generated carrier energy distribution that obeys the FD distribution. Under the condition of $\hbar\omega \gg E_f$ (Fermi energy), the carrier distribution can be simplified to the Maxwell-Boltzmann (MB) distribution [4, 26], leading to the expression

$$\Delta A(\hbar\omega) = -A_1 \exp\left(-\frac{\hbar\omega}{k_B T_e}\right), \quad (5.3)$$

where A_1 is a prefactor, k_B is the Boltzmann constant, and T_e is the carrier temperature.

Figure 5.3: Normalized transient absorption spectra with fluence of $\sim 83 \mu\text{J}/\text{cm}^2$ under (a) 400-nm pump and (c) 770-nm pump. Extracted carrier temperatures under (b) 400-nm pump and (d) 770-nm pump at respective pump fluences. Red solid lines in (a) and (c) are the MB fitting curves. Black solid lines in (b) and (d) are to denote 293 K.

By fitting the data in the range of 1.68–2 eV (400-nm pump, see Fig. 5.3a) and 1.65–1.8 eV (770-nm pump, see Fig. 5.3c) to Eq. 5.3, we obtain T_e as a function of time delay τ , as shown in Fig. 5.3b and 5.3d, respectively.

The 400-nm pump results are consistent with previous works, that is, the observation of slow carrier cooling under high pump fluences in this family of perovskite materials [4]. In contrast, the normalized $-\Delta A(\hbar\omega)$ after 770-nm pump shows a negligible change in carrier temperature (Fig. 5.3d), by fitting the data to the MB

distribution (Fig. 5.3c). Note that the $T_e(\tau)$ in Fig. 5.3d is slightly higher than the room temperature value of 293 K, and is the consequence of not taking into account the transient change in the reflection in the analysis of data [35].

5.2.3 Transient changes in bandgap and exciton binding energy

Next we analyze data over the entire spectral range to extract the other parameters, at each time delay. After photoexcitation, transient change in the bandgap result from BGR and band filling, which coexist and compete with each other [36]. Here we introduce a photoinduced change in bandgap (ΔE_g) to account for BGR, and insert the FD distribution (f_{FD}) in the conduction band (valence band) for electrons (holes) in the CC term,

$$\begin{aligned} \Delta A_{CC}(\hbar\omega) &= f_1 A'_{CC}(E'_b, E'_g, \hbar\omega)(1 - f_{FD})^2 - A_{CC}(\hbar\omega), \\ &= A_1 \frac{2\pi\sqrt{E'_b}}{\hbar\omega} \frac{1}{\Gamma} \int_{E'_g}^{\infty} \text{sech}\left(\frac{\hbar\omega - E}{\Gamma}\right) \frac{\xi(\hbar\omega - E'_g)}{1 - \exp(-2\pi\sqrt{\frac{E'_b}{E - E'_g}})} dE \\ &\quad \times \left(1 - \frac{1}{1 + \exp\left(\frac{\hbar\omega - E_f}{k_B T_e}\right)}\right)^2 - A_1 \frac{2\pi\sqrt{E_b}}{\hbar\omega} \frac{1}{\Gamma} \int_{E_g}^{\infty} \text{sech}\left(\frac{\hbar\omega - E}{\Gamma}\right) \\ &\quad \times \frac{\xi(\hbar\omega - E_g)}{1 - \exp(-2\pi\sqrt{\frac{E_b}{E - E_g}})} dE, \end{aligned} \quad (5.4)$$

where $E'_b \equiv E_b + \Delta E_b$, $E'_g \equiv E_g + \Delta E_g$, f_1 is a prefactor to account for the photoinduced change in μ_{cv}^2 , and $(1 - f_{FD})^2$ accounts for occupied transitions by carriers, due to the Pauli exclusion principle and characterized by the quasi-Fermi energy E_f and the carrier temperature T_e . Equation 5.4 assumes (1) the electron and hole effective masses are nearly the same, (2) a negligible photoinduced change in the nonparabolic parameter R , and (3) $T_e \approx T_h$, where T_h is the temperature of holes.

Next we consider the EC term. Considering the changes in E_b , Γ , and E_g after

photoexcitation, the photoinduced change in the EC term can be expressed as

$$\begin{aligned}
\Delta A_{EC}(\hbar\omega) &= f_1 f_2 A'_{EC}(E'_b, E'_g, \Gamma', \hbar\omega) - A_{EC}(\hbar\omega), \\
&= f_1 f_2 A_2 \frac{2\pi\sqrt{E'_b}}{\hbar\omega} \frac{1}{\Gamma'} \sum_{j=1}^7 \frac{2E'_b}{j^3} \operatorname{sech}\left(\frac{\hbar\omega - E'_g + \frac{E'_b}{j^2}}{\Gamma'}\right) \\
&\quad - A_2 \frac{2\pi\sqrt{E_b}}{\hbar\omega} \frac{1}{\Gamma} \sum_{j=1}^7 \frac{2E_b}{j^3} \operatorname{sech}\left(\frac{\hbar\omega - E_g + \frac{E_b}{j^2}}{\Gamma}\right),
\end{aligned} \tag{5.5}$$

where $\Gamma' \equiv \Gamma + \Delta\Gamma$ and f_2 is the factor to account for the ratio of exciton oscillator strength after photoexcitation to before photoexcitation [34]. The exciton oscillator strength is proportional to the transition probability of an electron going from the valence band state to an excitonic state [29, 34].

Figure 5.4: The upper panel shows (a) Experimental data (circles) and fits (dashed lines), (b) carrier contribution, and (c) excitonic contribution at different fixed temperatures. Extracted Fermi level energy is shown in (d). Carrier temperature used in fits are plotted in (e), including carrier temperature at 500 K, 700 K, and T_e obtained from MB fits.

Combining both the CC and EC terms, we then fit the transient absorption data

$\Delta A(\hbar\omega)$ to

$$\Delta A(\hbar\omega) = \Delta A_{CC}(\hbar\omega) + \Delta A_{EC}(\hbar\omega). \quad (5.6)$$

We found that E_f and T_e are dependent on each other, i.e., we can find different sets of (E_f, T_e) values that can fit the data equally well. This is a consequence of the fact that T_e and E_f appear only in the FD term via the exponent $\frac{\hbar\omega - E_f}{k_B T_e}$ in Eq. 5.6, and nowhere else, and that E_f will adjust itself depending on the value of T_e , to yield identical fits. For 770-nm pump, when T_e is fixed at (a) 500 K, (b) 700 K, or (c) T_e obtained from the MB fits, the fits quality are equally good (5.4a-c), with very different observed E_f values. To overcome the problem, since we have obtained T_e from the MB fits to the normalized $\Delta A(\hbar\omega)$ at high photon energies, we fix T_e (extracted from the MB fits in Eq. 5.3) to obtain E_f in the fits to Eq. 5.6. In Eq. 5.6, the fitting parameters are ΔE_g , ΔE_b , E_f , $\Delta\Gamma$, f_1 , and f_2 . We then plot $\Delta A_{CC}(\hbar\omega)$ and $\Delta A_{EC}(\hbar\omega)$, separately, to visualize the CC and EC terms at each time delay.

Figure 5.5 shows the CC and EC terms under 400-nm excitation at selected time delays. At 0.5 ps, the bleaching shows a sharp onset at 1.63 eV and a very broad high-energy tail. From Fig. 5.5b and 5.5c, we find that the sharp bleaching onset is contributed by both CC and EC terms, while the high-energy tail can only be attributed to the band filling of hot carriers described by the FD distribution. After several picoseconds, the bleaching dip contributed by carriers moves towards lower-energy states as the carriers lose energy while cascading down to the bandedge. At the same time, the bleaching amplitude near the bandedge becomes larger, suggesting the predominance of bandedge transitions (to both carrier and excitonic levels), which is the result of the large number of carriers cooling down to the bandedge. At long time delays (Fig. 5.5e), however, as carriers keep cooling down to bandedge, the bleaching contributed by carriers moves to even lower energies in the band. However now, the bleaching amplitude decreases with time delay due to carrier recombination. The EC term does not merely show the change in amplitude, but also in the linewidth and energies of lowest excitonic transitions which we can recognize from the dip

Figure 5.5: Experimental data (circles) and fits (dashed lines) (a–c) at short time delays and (d–f) long time delays for 400-nm pump. CC [EC] terms are shown in (b) and (e) [(c) and (f)].

position, as shown in Fig. 5.5c and 5.5f.

For 770-nm pump, we repeat the procedures to obtain Fig. 5.6, which shows the ΔA fits. The EC and CC changes slightly at short time delays (Fig. 5.6 b,e) and long time delays (Fig. 5.6 c,f). Figures 5.6b and 5.6e confirm that no hot carriers were generated with resonant excitation.

5.2.4 Unusual bandgap renormalization

In traditional semiconductors, such as a heavily Sn-doped In_2O_3 , the optical bandgap increases with carrier density N [37]. This bandgap widening is the combined effect of Burstein-Moss effect and bandgap renormalization, in which the latter contributes to bandgap reduction [37, 38]. Walsh *et al.* later revealed that the nonparabolic nature of the conduction band is a key contribution to this renormalization [36].

In ZnO nanocrystals, the bandgap decreases with increasing lattice temperature

Figure 5.6: Experiment data (circles) and fits (dashed line) at short time delays (a–c) and long time delays (d–f) for 770-nm pump. CC [EC] terms are shown in (b) and (e) [(c) and (f)].

[39]. However, lead halide perovskites exhibit an atypical temperature dependence of bandgap — the bandgap *increases* with increasing temperature [40, 41]. This temperature dependence of the bandgap in MAPbI₃ is attributed to both thermal expansion and electron–phonon interactions, of which the former predominantly contributes to the BGR [42]. This abnormal temperature dependence of the fundamental gap makes the sign of photoinduced change in bandgap uncertain — it is not entirely certain that BGR must result in a bandgap reduction in the perovskites.

Figures 5.7a and 5.7b show the time evolution of ΔE_g under 400-nm pump and 770-nm pump, respectively. Note that the ΔE_g term in Eq. 5.4 & 5.5 accounts for only BGR, and not the Burstein-Moss effect. In contrast to previous TA works [4, 26, 27], our extracted ΔE_g is positive at all time delays for all pump fluences, implying that the bandgap increases after photoexcitation. This is consistent with the temperature dependence of the bandgap [40, 41].

Figure 5.7: Extracted parameter—change in bandgap ΔE_g under (a) 400-nm and (b) 770-nm pump with fluence of $83 \mu\text{J}/\text{cm}^2$.

5.2.5 Carrier density and exciton oscillator strength

After photoexcitation, part of the conduction band (valence band) is occupied by photoexcited electrons (holes). These filled states lead to transient forbidden interband transitions, and so cannot contribute to the photogenerated carrier density N . With the assumption that the electron density is equal to the hole density, the electron density N_e can be a measure of carrier density N . The electron density N_e can be calculated from the extracted fitting parameters E_g , E_b , E_f , and T_e via the formula $N_e = \int_{E_g}^{\infty} D_c(\hbar\omega) f_{FD} d\hbar\omega$, where $D_c(\hbar\omega)$ is the density of states of conduction band [4]. The full expression is

$$N_e = \int_{E_g}^{\infty} \frac{1}{2\pi^2} \left(\frac{2m_{eff}}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E - E_g} \frac{\xi(E - E_g)}{1 + \exp((E - E_f)/k_B T_e)} dE \quad (5.7)$$

Figure 5.9a shows that the obtained electron density with a 400-nm pump decreases with time delay τ . We plot the inverse of the electron density ($1/N_e$) as a function of τ at a fluence of $\sim 69 \mu\text{J}/\text{cm}^2$ in Fig. 5.8b, and find it is linear from 2 ps and 80 ps, indicating that carrier recombination is predominantly second-order at these carrier densities. This finding agrees with reports of a linear relation between $(\Delta A)^{-1}$ at the bleaching wavelength and the time delay τ [22]. We fitted the data shown in the inset of Fig. 5.9a in the range of 2–1000 ps, and then extrapolated the fitting curve down to 0.5 ps. In the inset, we see that during the first 2 ps, the second-order recombination curve underestimates the electron density. This discrepancy can

Figure 5.8: (a) Fluence-dependent $1/N_e$ with 400-nm pump. (b) The $1/N_e$ is linear between 2 and 80 ps at fluence of $\sim 69 \mu\text{J}/\text{cm}^2$. The inset figure in (b) shows $1/N_e$ between 0.5 ps and 80 ps.

be explained by the process of exciton formation leading to decreasing free carrier population, which we will see later when we analyze the exciton dynamics.

Figure 5.9: (a) Extracted electron density N_e and (b) f_2 (exciton oscillator strength after to before optical excitation) under 400-nm pump with different pump fluences. The inset figure in (a) presents extracted N_e (blue triangles) and a second-order recombination fit (black solid line) with a fluence of $\sim 69 \mu\text{J}/\text{cm}^2$ with an arrow to denote 2 ps.

We next try to understand the time evolution of the extracted fitting parameter $f_2(\tau)$. According to Eq. 5.5, the factor f_2 is defined as the ratio of exciton oscillator strength after to before optical excitation. Figure 5.9b shows f_2 as a function of time after photoexcitation. We see that f_2 decreases below 1, and reaches a minimum at about 10 ps, and rises back up to approach 1 at long time delays. The data therefore indicates a decrease of the transition probability to an excitonic state due

to photoexcitation with minimum of ~ 10 ps. Note that our f_2 value of ~ 0.8 at 10 ps at a fluence of $\sim 14 \mu\text{J}/\text{cm}^2$ agrees with that in MAPbI₃ [4], though ours is the first work to show the *non-monotonic* excitonic density with a time delay after photoexcitation.

Another interesting point in Fig. 5.9b is that f_2 is a strong function of pump fluence, at a fixed time delay. Figure 5.9b shows f_2 as a function of fluence at different time delays. This suggests the use of fluence to control the exciton populations, depending on the functionality we wish the perovskite devices to exhibit.

5.3 Discussions and Conclusions

We employ the model that Saba *et al.* used to fit steady-state absorption data, in *both* steady-state absorption spectra and transient absorption spectra [33]. This allows us to fit the steady-state absorption spectra over a larger energy range, which makes our fits to transient absorption spectra more reliable and convincing. The positive photoinduced change in E_g , though not agreeing with previous reports on perovskites [4, 26, 27] nor with the negative BGR in traditional inorganic semiconductors like GaAs [43, 44], is however consistent with the “abnormal” positive thermal expansion coefficient observed experimentally [40, 41]. We believe that the nonparabolic nature of the bands is a key assumption to fully elucidate the transient absorption spectra.

Secondly, we have extracted the time evolution of key fitting parameters from 0.5 ps to 1 ns. With the proper model, we are able to disentangle CC and EC at each pump-probe delay, that enables us to visualize the carrier and exciton dynamics sequentially. We can now resolve the time evolution of the carrier and exciton oscillator strength. At high pump fluences and short time delays, exciton states are occupied due to exciton formation after photoexcitation, while the f_2 is weaker and short-lasting at low pump fluences. These observations suggest the use of pump fluence as a “knob” to control the exciton populations and hence the carrier-to-exciton conversion efficiencies, so that we can use lead halide perovskites in various

applications from photovoltaic to lasing.

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Chapter 6

Exploring carrier dynamics in dual-phase $\text{CsPbBr}_3\text{--CsPb}_2\text{Br}_5$ thin films using time-resolved terahertz spectroscopy

Dual-phase $\text{CsPbBr}_3\text{--CsPb}_2\text{Br}_5$ thin films are reported with superior photovoltaic performance. We performed TRTS measurements on the dual-phase $\text{CsPbBr}_3\text{--CsPb}_2\text{Br}_5$ thin films to detect the photophysics after photoexcitation. Using a combination of the Drude-Smith model and the Peak-Shift model to fit the photoconductivity spectra, we extracted the carrier dynamics, and found a third-order dominated carrier recombination kinetics, moderate carrier mobility and low diffusion length, indicating there is still room for improvement in this material system.

6.1 Introduction

All-inorganic perovskite CsPbBr_3 has been under intense research as photovoltaic, light-emitting, and lasing devices [1–3]. The advantages of CsPbBr_3 include not only its high luminescence quantum yield and robust thermal stability but also its

easy and low-cost fabrication using solution processing techniques. However, there are by-products including Cs_4PbBr_6 and CsPb_2Br_5 in the obtained CsPbBr_3 [4, 5]. The CsPbBr_3 crystal has corner shared $[\text{PbBr}_6]^{-4}$ octahedra in the crystal structure (see Fig. 6.1b) and possesses a bandgap of ~ 2 eV [6].

Figure 6.1: Schematic view of the crystalline structures of (a) Cs_4PbBr_6 , (b) CsPbBr_3 and (c) CsPb_2Br_5 . Taken from Ref. [5].

In the Cs_4PbBr_6 compounds, $[\text{PbBr}_6]^{-4}$ octahedra are isolated and separated by Cs ions as shown in Fig. 6.1a. The optical properties are dominated by transitions *within* the individual octahedron, hence it is called a zero-dimensional perovskite [7]. Cs_4PbBr_6 , on the other hand, shows a large bandgap ~ 4 eV due to the negligible orbital overlapping between adjacent octahedra [8, 9]. Another possible by-product in the preparation of CsPbBr_3 is CsPb_2Br_5 . Figure 6.1c shows the crystalline structure of CsPb_2Br_5 . The crystal CsPb_2Br_5 possesses a two-dimensional (2D) structure with Cs^{+1} ions sandwiched by $[\text{Pb}_2\text{Br}_5]^{-1}$ polyhedral layers [4]. The lattice parameters originally reported by Cola *et al.* suggest that CsPb_2Br_5 possesses a body-centered tetragonal structure [10, 11]. Density functional theory (DFT) results show that 2D CsPb_2Br_5 possesses an indirect bandgap of ~ 3.1 eV at the Γ point [6, 12].

Li *et al.* compared the XRD patterns and the absorption spectra of CsPbBr_3 (Fig. 6.2a and Fig. 6.2b), Cs_4PbBr_6 (Fig. 6.2c and Fig. 6.2d) and CsPb_2Br_5 (Fig. 6.2e and Fig. 6.2f), respectively [13]. CsPbBr_3 shows a characteristic peak at $\sim 15^\circ$ [2θ , the powder diffraction file (PDF) number is PDF#18-0364] while Cs_4PbBr_6 has a peak at $\sim 12.6^\circ$ (PDF#73-2478) and CsPb_2Br_5 at $\sim 11.6^\circ$ (PDF#25-0211). It should be noted here that one can differentiate CsPbBr_3 in different phases via their XRD peaks between 15° and 30° . Cubic CsPbBr_3 presents overlapping peaks

at $\sim 15^\circ$, $\sim 21.5^\circ$, $\sim 26.5^\circ$, and $\sim 30.6^\circ$ (PDF#54-0752), while tetragonal CsPbBr_3 presents overlapped peaks at $\sim 15.2^\circ$, $\sim 21.5^\circ$, and $\sim 30.6^\circ$ [data found in the inorganic crystal structure database (ICSD) with ICSD # 109295], and orthorhombic CsPbBr_3 shows a series of peaks between 15 and 30° , which are distinct from the other ternary Cs-Pb-Br systems (PDF#18-0364). The absorption spectra of the three systems show obvious differences because of their different bandgap (see Fig. 6.2) [13, 14]. Figure 6.2f indicates that the 2D CsPb_2Br_5 shows a bandgap of 3.1 eV (400 nm). The optical properties of the ternary Cs-Pb-Br systems with mixed phases (i.e. dual-phase CsPbBr_3 - CsPb_2Br_5 system) are the combination of that of each phase [5]. Acharyya *et al.* showed that the absorption spectra of dual-phase CsPbBr_3 - CsPb_2Br_5 systems contains bandgap properties of both CsPbBr_3 and CsPb_2Br_5 [6]. It is thus easy to differentiate the presence of CsPbBr_3 from CsPb_2Br_5 with the aid of absorption spectra and XRD.

The three ternary Cs-Pb-Br compounds CsPbBr_3 , CsPb_2Br_5 and Cs_4PbBr_6 can be converted from one to another via controlling the growth conditions [6, 13, 15, 16]. In the ideal case, the precursors CsBr and PbBr_2 to fabricate CsPbBr_3 should have a molar ratio of 1:1. CsPb_2Br_5 can be formed with excess PbBr_2 [6] while Cs_4PbBr_6 can be formed with excess CsBr [15]. The reverse conversion from Cs_4PbBr_6 and CsPb_2Br_5 to CsPbBr_3 can be realized via water extraction and thermal annealing [13].

It has been reported that the existence of one kind of by-product (Cs_4PbBr_6 or CsPb_2Br_5) in CsPbBr_3 can enhance its optoelectronic performance in LED and solar cell devices [16–19]. The presence of CsPb_2Br_5 in CsPbBr_3 film gives rise not only to long-term thermal stability, but also large grain size [19, 20], resulting in a high power conversion efficiency (PCE). However, there are contradictory reports on whether the presence of CsPb_2Br_5 can improve the photovoltaic performance of CsPbBr_3 . Li *et al.* reported a long-time stability for more than 1000 h (45% humidity) and a PCE of 8.34% in the dual-phase CsPbBr_3 - CsPb_2Br_5 thin film prepared with the ratio of CsBr to PbBr_2 1:1.1 in the vapor system [20]. On the other hand, Liu *et al.* reported

Figure 6.2: XRD patterns and absorption spectra of the ternary Cs-Pb-Br systems. XRD patterns of (a) CsPbBr_3 , (c) Cs_4PbBr_6 , and (e) CsPb_2Br_5 . Corresponding absorption spectra are shown in (b), (d) and (f), respectively. Standard PDF data are plotted in (a), (c) and (e), respectively. Peak denoted with purple dot in (c) is to characterize CsBr. Taken from Ref. [13].

a long-time stability for 200 days (25–85% humidity, 20–30°C) and a PCE of 6.1% of CsPbBr_3 thin film with only tiny amounts of CsPb_2Br_5 [16], suggesting that samples with the least amount of CsPb_2Br_5 showed the highest PCE and long-term stability, and so using high-quality CsPbBr_3 can increase the photovoltaic performance. The above two contradictory results maybe due to the following reasons: (1) the amounts of CsPb_2Br_5 in the CsPbBr_3 layers in the two papers are not clear, and (2) the different growing methods induced surface morphology difference. Compared to the vapor method used in Ref. [20], Liu *et al.* used the solution method, and dipped the porous CsPb_2Br_5 layer into CsBr precursor solution to obtain the CsPbBr_3 layer. On the other hand, a larger PCE up to 9.43% of the pure CsPbBr_3 was

reported by Duan *et al.* after interfacial modification and plasma treatment [21]. Their sample (without encapsulation) show a long-time stability over 40 days (80% humidity, 20°C) [21]. Ultrafast measurements on these samples can unravel the possible reasons for the comparable PCEs of these dual- and single-phase materials.

When characterizing the charge transport of halide perovskites, low-lying phonon modes can interact with charge carriers and thus modify the obtained charge transport properties [22]. Having a knowledge of the low-lying phonon modes is crucial in disentangling phonon from carrier dynamics [22]. Low-frequency Raman scattering spectra and the infrared (IR) spectroscopy are both powerful tools in detecting low-lying phonon modes. For any IR-active absorption, the vibrational excitation must change the dipole moments of the perovskites for the absorption of IR radiation to occur. For Raman scattering, the mechanism giving rise to Raman-active phonon modes is a change in the polarizability of the crystal as it vibrates [23]. Therefore, considering the possible symmetry of a crystal, a low-lying phonon mode could be active in IR-active, Raman-active, both, or neither. Typically, in a bulk material, Raman-active phonon modes possess symmetric vibrations because of the possible change in polarizability, while IR-active phonon modes possess asymmetric vibrations because of the possible change in dipole moment [23].

Low-frequency Raman scattering spectroscopy has been performed to characterize the ternary Cs-Pb-Br systems [24, 25]. Yaffe *et al.* reported Raman scattering spectra of CsPbBr₃ in the orthorhombic (80 K), tetragonal (400 K), and cubic (500 K) phases [24]. Their Raman spectra of CsPbBr₃ in the orthorhombic phase shows two sharp peaks at ~ 30 and 48 cm^{-1} , consistent with the DFT results [24]. The same DFT calculations also predicted two IR-active phonon modes at ~ 28 and $\sim 39\text{ cm}^{-1}$ and one Raman-active phonon mode at $\sim 31\text{ cm}^{-1}$ [24]. On the other hand, for CsPbBr₃ in the cubic phase, Yaffe *et al.* can only obtain diffuse spectra composed of a broad feature arising from structural disorder below 50 cm^{-1} [24]. According to theoretical calculation, the Raman-active phonon modes of halide perovskites below 100 cm^{-1} are attributed to the octahedra (twist or distortion) [26, 27].

Low-frequency Raman scattering spectroscopy can be used to detect a small amount of CsPbBr_3 in CsPb_2Br_5 . Figure 6.3b indicates that at low temperature (80 K), there are no tetragonal CsPb_2Br_5 Raman peaks below 40 cm^{-1} , while orthorhombic CsPbBr_3 shows Raman peaks at 28 and 32 cm^{-1} . Thus, at 80 K, even with tetragonal CsPb_2Br_5 present, the presence of orthorhombic CsPbBr_3 can be monitored via Raman peaks at 28 and 32 cm^{-1} [25]. At room temperature, the Raman spectrum of tetragonal CsPbBr_3 shows a broad feature due to dynamic disorder (dashed line in Fig. 6.3a). The Raman spectrum of CsPb_2Br_5 in the tetragonal phase [10] also does not show any peaks below 40 cm^{-1} at room temperature. Hadjiev *et al.* predicted that the tetragonal CsPb_2Br_5 possesses IR-active phonon modes at 18 and 46 cm^{-1} [25]. Knowing the locations of these low-lying phonon modes is helpful in the analysis of TRTS data of these materials.

Figure 6.3: Raman spectra of CsPb_2Br_5 and CsPbBr_3 at (a) 295 and (b) 80 K. The dashed line in (a) depicts the dynamic-disorder induced central peak in CsPbBr_3 at high temperature [24]. Taken from Ref. [25]

In a THz-TDS measurement, THz photons can be absorbed by either the carriers

or phonon modes. With photoexcitation, one can disentangle phonon mode from carrier dynamics with the aid of TRTS. Using TRTS, Zhao *et al.* observed a delicate interplay among carriers, phonons, and excitons in the mixed-cation mixed-halide perovskites [22]. In this chapter, ternary Cs-Pb-Br systems were grown and characterized by XRD and THz-TDS. Then THz-TDS and TRTS measurements were performed on dual-phase CsPbBr₃-CsPb₂Br₅ thin films to explore photoexcited carrier and low-lying phonon dynamics.

Ternary Cs-Pb-Br thin films were grown on single-crystal substrates using pulsed laser deposition technique by our collaborator Cheng Shijia from Professor Sun Handong's group. MgO substrates were chosen for the growth of ternary Cs-Pb-Br systems while NaCl substrates were chosen for the growth of the specific dual-phase CsPbBr₃-CsPb₂Br₅ thin films for TRTS measurements. For the dual-phase CsPbBr₃-CsPb₂Br₅ thin films grown for TRTS measurements, (1) CsPbBr₃ targets were compressed mixtures of CsBr and PbBr₂ with a molar ratio as 1:2 and (2) CsPbBr₃ target surfaces were perpendicular to the direction of the laser pulses. With CsPbBr₃ target surfaces parallel or perpendicular to the direction of the laser pulses, together with a changing target molar ratio from 1:1, 1:1.5 to 1:2, six kinds of perovskite films with different compositions were obtained. The thicknesses of the dual-phase films were controlled by varying the growth time.

6.2 Results and discussion

The six kinds of ternary Cs-Pb-Br thin films are grown on MgO substrates. The ternary systems have different crystal structures and hence different XRD patterns and THz transmittance spectra. Before the THz-TDS measurements on the ternary Cs-Pb-Br samples, we measured the MgO substrates with THz-TDS (see Fig. 6.4a and b), and extracted the n and k of the substrates for further extraction of n and k of the samples via Eq. 2.3, and subsequently obtaining optical conductivity of the samples. Using XRD patterns, the existence of CsPbBr₃ can be recognized via its characteristic peak at $\sim 15^\circ$, with hexagonal Cs₄PbBr₆ at $\sim 12.6^\circ$ and tetragonal

Figure 6.4: Extracted (a, c) n and (b, d) k of MgO and NaCl crystal substrates, respectively.

CsPb₂Br₅ at $\sim 11.6^\circ$. One can recognize the phase of CsPbBr₃ from the peaks at larger than 15° . Figure 6.5a shows Batch 2, 3, and 5 are combinations of tetragonal CsPb₂Br₅ and orthorhombic CsPbBr₃ because of the existence of characteristic peaks at $\sim 11.6^\circ$ and $\sim 15^\circ$. The determination of orthorhombic CsPbBr₃ arises from the series of XRD peaks between 20 and 30° . Since orthorhombic CsPbBr₃ possesses IR-active phonon modes at ~ 28 and ~ 39 cm^{-1} [24] and tetragonal CsPb₂Br₅ possesses IR-active phonon modes at 18 , 46 , and 58 cm^{-1} [25], the phonon modes at ~ 1 THz of Batch 2, 3 and 5 should be assigned to orthorhombic CsPbBr₃ (Fig. 6.5b). Phonon modes larger than 1 THz could be overlapping phonon modes from both orthorhombic CsPbBr₃ and tetragonal CsPb₂Br₅. XRD patterns of Batch 1, 4, and 6 in Fig. 6.5a show characteristic XRD peaks at $\sim 12.6^\circ$ indicating the existence

of hexagonal Cs_4PbBr_6 . Motti *et al.* reported their bulk CsPbBr_3 in the cubic phase possessing broadband absorption spectra between 1 and 5 THz peaked at ~ 2.3 THz [28]. Their THz-TDS results are consistent with the existence of cubic CsPbBr_3 in Batch 1, 4, and 6 (Fig. 6.5b) of our samples, which show broadband absorption peaked around 2 THz in our THz-TDS spectra.

Figure 6.5: (a) XRD patterns and (b) THz transmittances of ternary Cs-Pb-Br systems with six different compositions with labels from Batch 1 to Batch 6. Batch 1 (Batch 3/5) and 2 (Batch 4/6) were grown (1) with CsPbBr_3 target molar ratio as 1:2 (1:1.5/1:1) and (2) with target surface parallel and perpendicular to laser pulses.

To prove the presence of tetragonal CsPb_2Br_5 in the obtained ternary Cs-Pb-Br systems, Batch 2 was chosen to be annealed so that tetragonal CsPb_2Br_5 could be converted to CsPbBr_3 . XRD patterns (Fig. 6.6) show that upon annealing, signals of crystalline CsPb_2Br_5 is weaker and XRD patterns of CsPbBr_3 is stronger compared to that before annealing, indicating a well crystalline CsPbBr_3 . Figure 6.6b shows a broadband absorption peaked at ~ 2.5 THz of the sample after annealing, indicating the presence of the cubic CsPbBr_3 [28]. The THz transmittance spectra show that the phonon mode at 1 THz of the sample before annealing, which is arising from orthorhombic CsPbBr_3 , disappears after annealing, and is converted to the cubic CsPbBr_3 .

Cinquanta *et al.* reported transient a blue shift of phonon modes [27, 42, 57, and 63 cm^{-1} (i.e., ~ 0.82 , ~ 1.27 , ~ 1.73 , and ~ 1.91 THz, respectively)] in CsPbBr_3 films upon photoexcitation using TRTS [29]. Because of the high transition temperatures of ternary Cs-Pb-Br systems, no systematic THz-TDS results of the Cs-Pb-Br system

Figure 6.6: (a) The XRD pattern and (b) THz transmittance of the dual-phase CsPbBr_3 - CsPb_2Br_5 thin film before and after annealing at 400°C for 4h following procedures described in Ref. [13].

in structural phases have been reported. Shi *et al.* measured CsPbBr_3 with micro-cube size using THz-TDS and found that THz absorption spectra of the micro-cube were a combination of four phonon modes peaked at 0.97, 1.39, 1.95, and 2.38 THz, respectively. They attributed the phonon mode at 0.97 THz to the stretching of the Pb-Br bond in orthorhombic CsPbBr_3 [30]. The phonon mode at 1.39 THz was attributed to the octahedra distortion in tetragonal CsPb_2Br_5 which is consistent with the calculated IR-active phonon mode at 46 cm^{-1} ($\sim 1.39\text{ THz}$) by Hadjev *et al.* using DFT [25]. Hadjev *et al.* also predicted possible IR-active phonon modes in tetragonal CsPb_2Br_5 at 58, 60, and 73 cm^{-1} (i.e., ~ 1.75 , 1.82, and 2.21 THz, respectively) [25]. Moreover, Yaffe *et al.* predicted IR phonon modes of orthorhombic CsPbBr_3 at ~ 28 and $\sim 39\text{ cm}^{-1}$ (~ 0.85 and $\sim 1.18\text{ THz}$) using DFT [24]. In conclusion, one should note the possible overlapping of phonon modes arising from orthorhombic CsPbBr_3 and tetragonal CsPb_2Br_5 between 1.3 and 2.3 THz especially when the possibility of the existence of mixed-phase ternary Cs-Pb-Br system is large.

Phonon modes located between 1.3 and 2.3 THz can be contributed by both orthorhombic CsPbBr_3 and tetragonal CsPb_2Br_5 . The phonon mode contributions between 1.3 and 2.3 THz are complicated. As a result, we will only analyse phonon modes outside this frequency window, i.e., phonon mode at 1 THz that are arising

from orthorhombic CsPb_2Br_5 .

For further TRTS measurements, the dual-phase CsPbBr_3 – CsPb_2Br_5 thin film on NaCl substrate was grown with a thickness of ~ 427 nm using the same growth method as for Batch 2. NaCl substrate is selected due to good lattice matching between NaCl and CsPbBr_3 , at the expense of the signal-to-noise ratio of TRTS data. To obtain n and k of the perovskite samples, we extracted n and k of NaCl (see Fig. 6.4c and d). THz transmittance is high at 20 K and low at 285 K. One can determine the trustable region in TRTS measurements from the real ($\Delta\sigma_1$) and imaginary ($\Delta\sigma_2$) parts of the photoconductivity of samples with “no pump” — $\Delta\sigma_1$ and $\Delta\sigma_2$ should be zero. Figure 6.7 shows the real part of photoconductivity with no pump at 20 and 285 K. Hence, at low temperature, the trustable region is 0.3–1.9 THz (Fig. 6.7a), while at high temperature, the trustable region is 0.3–1.5 THz (Fig. 6.7b).

Figure 6.7: The photoconductivity $\Delta\tilde{\sigma}$ with no pump at (a) 20 and (b) 285 K. The averaged real and imaginary parts of photoconductivity (from 10 runs) at 20 K are flat between 0.3 and ~ 1.9 THz, and the averaged $\Delta\sigma_1$ and $\Delta\sigma_2$ at 285 K are totally flat between 0.3 and ~ 1.5 THz.

The film for TRTS measurements shows XRD patterns to be a combination of both CsPbBr_3 and CsPb_2Br_5 which is similar to Batch 2 (see Fig. 6.8). The THz transmittance spectrum of the film (Fig. 6.8) shows phonon modes at ~ 1 , ~ 1.5 , and ~ 2 THz.

We can extract the complex photoconductivity at a series of well-defined pump–

Figure 6.8: (a) XRD patterns and (b) THz transmittance spectra for dual-phase CsPbBr₃-CsPb₂Br₅ on NaCl substrate.

probe time delays. Figure 6.9 shows the extracted photoinduced change in complex conductivities at 20 and 285 K, respectively. The Drude-Smith response in transient complex conductivity spectra have been found in heavily-disordered perovskites [31–33]. Our obtained complex conductivity spectra show a derivative-like feature of a Lorentzian lineshape near the phonon mode frequency on top of a Drude-Smith feature. The peak-shift contribution to photoconductivity $\Delta\tilde{\sigma}(\omega)$ has the derivative form of the Lorentzian function which was first reported by Zhao *et al.* [22]. Therefore, the equation to fit photoconductivity data has the expression

$$\Delta\tilde{\sigma}(\omega) = \Delta\tilde{\sigma}_{DS}(\omega) + \Delta\tilde{\sigma}_{PS}(\omega). \quad (6.1)$$

The Drude-Smith term $\Delta\tilde{\sigma}_{DS}(\omega)$ and the peak-shift term $\Delta\tilde{\sigma}_{PS}(\omega)$ have the expressions

$$\Delta\tilde{\sigma}_{DS}(\omega) = \left(1 + \frac{c_1\gamma}{\gamma - i\omega}\right) \frac{\epsilon_0\omega_p^2}{\gamma - i\omega}, \quad (6.2)$$

$$\Delta\tilde{\sigma}_{PS}(\omega) = \frac{\epsilon_0\omega}{i(\omega_{p,j}^2 - \omega) + \omega\gamma_j} \Delta\omega_{p,j}^2 + \frac{-2i\omega_{0j}\epsilon_0\omega_{p,j}^2\omega}{[i(\omega_{p,j}^2 - \omega^2) + \omega\gamma_j]^2} \Delta\omega_{0j} - i\epsilon_0\omega\Delta\epsilon_\infty, \quad (6.3)$$

where c_1 is the fraction of carriers that retained their initial velocity after one collision event, γ is the scattering rate of carriers, ϵ_0 is the vacuum permittivity, ω_p is the plasma frequency, ω_{0j} is the frequency of the j^{th} oscillator, $\omega_{p,j}^2$ is the j^{th} oscillator strength, γ_j is the damping rate of the j^{th} oscillator, $\Delta\omega_{0j}$ is the photoinduced change

in ω_{0j} , and $\Delta\omega_{p,j}^2$ is the photoinduced change in $\omega_{p,j}^2$. It should be noted here that parameters ω_{0j} and $\omega_{p,j}^2$ are extracted from fits to optical conductivity at equilibrium with a combination of three oscillators. The oscillators are modeled with the Lorentz model. The Lorentz model has the expression

$$\tilde{\sigma}_L(\omega) = -i\epsilon_0\omega(\epsilon_\infty - 1) + \sum_j \frac{\epsilon_0\omega_{pj}^2\omega_j}{\gamma_j\omega + i(\omega_{0j}^2 - \omega^2)}, \quad (6.4)$$

where ϵ_∞ is the permittivity contributed from dielectric response beyond our frequency window. Therefore, using equation 6.1 to fit the photoconductivity spectra, fitting parameters ω_p^2 , c_1 , γ , $\Delta\omega_j$, and $\Delta\omega_{p,j}^2$ (Because I only focus on the phonon mode at ~ 1 THz, $j = 1$ thereafter) can be extracted simultaneously. Thereafter, we can disentangle the carrier contribution and phonon mode contribution to the photoconductivity, and then extract carrier dynamics in the disordered perovskite system

Figure 6.9: TRTS results: Complex photoconductivity at (a,b) 20 K and (c,d) 285 K. The fits are plotted in solid lines.

Next I calculate carrier density $N(t_{pp})$ as a function of defined pump-probe time delay t_{pp} via obtained plasma frequency (as described in Eq. 4.2). Carrier recombination can occur via radiative or nonradiative processes. The recombination of free carriers generally follows rate equation

$$\frac{d}{dt_{pp}} N(t_{pp}) = -[k_1 N(t_{pp}) + k_2 N^2(t_{pp}) + k_3 N^3(t_{pp})], \quad (6.5)$$

Figure 6.10: (a, c) The inverse of calculated $N(t_{pp})^2$ and (b, d) carrier density as a function of time delay at (a, b) 20 and (c, d) 285 K. (a) and (c) show the inverse of $N(t_{pp})^2$ at 20 and 285 K up to 1000 ps. The inset figures in (a) is the linear fit between 1.5 and 600 ps at 20 K, while at 285 K the linear range is between 1.5 ps and 800 ps. Red lines in (b) and (d) are third-order recombination curves.

where k_1 , k_2 , and k_3 are the monomolecular, bimolecular, and trimolecular recombination rate constants, respectively. The inverse of $N^2(t_{pp})$ for both 20 and 285 K (Fig. 6.10a and Fig. 6.10c) are linear to time delay t_{pp} , indicating a third-order predominant recombination process at both low and room temperatures with slope $2k_3$. From the linear fits, the extracted third-order rate constant $k_3 = (4.21 \pm 0.26) \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$ at 20 K, while $k_3 = (2.35 \pm 0.89) \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$ at 285 K. The obtained values of k_3 are comparable to the published values (e.g., third-order recombination rate is $(3.14 \pm 0.18) \times 10^{-23} \text{ cm}^6 \text{ s}^{-1}$ in colloidal CsPbBr_3 at room temperature) [31], which is about two orders larger than the Auger-recombination suppressed sample (e.g., third-order recombination rate is $(2.1 \pm 0.2) \times 10^{-25} \text{ cm}^6 \text{ s}^{-1}$ in colloidal CsPbBr_3) [32].

Figure 6.11: Extracted effective mobilities as a function of time delay at (a) 20 and (b) 285 K. Effective mobility at 20 K begins to cross zero from 30 ps, while crosses zero from $t_{pp} > 100$ ps at 285 K. The dashed line boxes indicate the trustable regions.

The effective mobility μ_{eff} in the Drude-Smith model can be extracted via Eq. 2.29. Figure 6.11 shows the effective mobility at both 20 and 285 K. The obtained effective mobility μ_{eff} reach a constant after ~ 10 ps with a value of $\sim 300\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at both 20 and 285 K, which are of the similar order of the published one on perovskite thin film (e.g. $\mu_{eff} \sim 400\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 15 K in MAPbI_3 thin film [32]). The extracted μ_{eff} show large fluctuation at long time delays, hence we trust the μ_{eff} values only in the regions indicated by the dashed boxes shown in Fig. 6.11.

Figure 6.12: Extracted diffusion length as a function of time delay at 20 (black squares) and 285 K (red dots). The curves are plotted according to the trustable regions of effective mobility at different temperatures.

The carrier diffusion length L_D can be calculated via Eq. 2.13. Figure 6.12 shows the extracted diffusion length at 20 K and 285 K. The extracted diffusion length is smaller than 100 nm at short time delay for both temperatures. Compared to the published ones $\sim 1\mu\text{m}$ of HOIP samples (e.g. MAPbBrI₃ thin film) [32, 34, 35], the dual-phase sample shows a much smaller diffusion length. The small diffusion length is believed to be related to the large Auger recombination [32]. Compared to the extracted values at 20 K, our extracted μ_{eff} and L_D are slightly larger at 285 K, which may arise from the composition differences in the dual-phase sample at different working temperatures.

6.3 Conclusion

Using XRD patterns and THz-TDS, we analyzed samples with different compositions. The 1-THz phonon mode in THz-TDS spectrum is finally attributed to the orthorhombic CsPbBr₃. Using TRTS at 20 and 285 K, we subtracted carrier contribution to the photoconductivity. The Auger recombination dominated carrier recombination process, a moderate carrier mobility but a small diffusion length in the dual-phase thin film have been revealed. We noted that the diffusion length and carrier mobility are slightly larger at 285 K, compared to that at 20 K, which can be attributed to the compositions differences at different temperatures. Though the dual-phase CsPbBr₃-CsPb₂Br₅ thin film is claimed to have high stability and good photovoltaic performance when it is compared to CsPbBr₃, from our TRTS measurements, we can see that there is still room in improving these dual-phase samples.

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Chapter 7

Conclusions

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

Our works aim at using ultrafast techniques including TRTS and TA spectroscopy to unveil the dynamics of carriers, excitons, and phonons modes, and thus to extract carrier dynamics in perovskites after photoexcitation. From TRTS, we can obtain carrier dynamics and thus extract carrier recombination constants to characterize the transport parameters in the samples. From TA, we can obtain both time-resolved carrier and exciton dynamics to extract both charge carrier and exciton properties.

Our first work is the TRTS measurements on overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ and stoichiometric CsPbI_2Br thin films. Using the Drude-Smith model to fit the photoconductivity, we extracted carrier dynamics after photoexcitation. Our TRTS results reveal that, compared to CsPbI_2Br , the better photovoltaic performance overstoichiometric $\text{Cs}_{1.2}\text{PbI}_2\text{Br}_{1.2}$ is due to: (1) a larger carrier density, (2) a similar mobility, and (3) a higher photon-to-carrier quantum yield at short time delays.

Our second work is TA measurements on the mixed-cation lead mixed-halide $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.97}\text{Br}_{0.03})_3$ thin films. Considering the nonparabolic nature of the bands, we adopted a high order coefficient to in the fitting model to both the steady-state absorption and TA data, which enlarges our fitting range. Our fitting results to TA data showing a positive photoinduced change in the electronic bandgap, though

disagreeing with previous reports on perovskites, but is consistent with the positive thermal expansion coefficient observed experimentally. We have extracted the time evolution of the key fitting parameters from subpicosecond to nanosecond scale. We are able to disentangle the carrier contribution and the excitonic contribution at each pump-probe delay, that enables us to visualize the time-resolved carrier and exciton contributions. We can see that the pump fluence is a useful “knob” to manipulate exciton oscillator strength, which enables us to use lead halide perovskites in various applications from photovoltaic to lasing.

Our third work using a combination of XRD, THz-TDS, and TRTS, on all-inorganic Cs-Pb-Br mixture systems. The THz-TDS measurements on the Cs-Pb-Br systems showed that the low-lying 1-THz phonon mode is attributed to the orthorhombic CsPbBr_3 . We performed TRTS measurements on a CsPbBr_3 – CsPb_2Br_5 dual-phase thin film. Using a combination of the Drude-Smith model and the Peak-Shift model, we are able to disentangle the carrier contributions from the 1-THz phonon contributions to photoconductivity. Though the CsPbBr_3 – CsPb_2Br_5 dual-phase thin film was claimed to have large PCE, our TRTS results reveal that the dual-phase thin film shows a diffusion length that is smaller than 100 nm, effective mobility smaller than $400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and a Auger recombination dominated carrier recombination.

Chapter 8

Future Work

We suggest the study of the dynamics of carriers, excitons, and phonon modes — the three degrees of freedom in halide perovskites and other novel materials. To manipulate the phonon modes, an intense THz pump is needed. Combined with THz probe from TRTS or broadband photon probe from TA, the intense THz pump will help to unveil the dynamics of carriers, excitons, and phonon modes in lead halide perovskites including chiral perovskites. Considering the potential applications of chiral perovskites, we propose using TA, time-resolved optical Kerr effect spectroscopy (TR-OKE) and TRTS, to characterize them.

8.1 Intense THz pump

Efficient high-power THz pulses allow for studies of nonlinear optical response of semiconductors with low-photon-energy excitations [2, 3]. The nonlinear crystal LiNbO₃ yields intense THz pulses via optical rectification with femtosecond (fs) pulse excitation, because of its large electro-optic coefficient ($d_{33} = 27$ pm/V) and its high optical transparency over a broad spectral range (350–5200 nm).

According to Ref. [1], the generation of intense single-cycle THz pulses from LiNbO₃ crystals uses the tilted-pump-pulse-front scheme to fulfill the phase-matching

Figure 8.1: (a) Schematic of intense THz pulse generation based on LiNbO₃ with a tilted-pump-pulse-front scheme. A grating is used to generate a tilted-pulse front. Two cylindrical lenses (L1 and L2, with focal lengths f_1 and f_2 , respectively) are used to form a $4f$ -lens configuration to ensure the spatial overlap among all frequency components. The LiNbO₃ crystal has prism angle $\theta_{LN} = 62^\circ$. THz pulses are generated at the surface with an angle between the incident optical pulsed. (b) Schematic of the THz pump with three parabolic mirrors (PM1, PM2, and PM3). Taken from Ref. [1].

condition, as shown in Fig. 8.1a. The phase-matching condition follows

$$v_g^{opt} \cos \theta = v_{THz}, \quad (8.1)$$

where v_g^{opt} is the group velocity of the optical pulse, θ is the angle to be tilted, and v_{THz} is the phase velocity of the THz pulse. The tilted front arise from the difference between group velocity of the optical pulse (c/v_g^{opt} , with $n_g^{opt} \approx 2.3$ in a LiNbO₃ crystal) and the phase velocity of the THz pulse (c/v_{THz} , with $n_{THz} \approx 5.2$ at 780 nm). The angle θ should be same as the prism angle θ_{LN} for the generated THz pulses coming out perpendicular to the LiNbO₃ surface. With a $4f$ -lens configuration, a maximum THz electric field of 1.2 MV/cm was obtained by Hirori *et al.* (see Fig. 8.1a) [1].

An intense THz pulse with an electric field amplitude larger than 1 MV/cm can drive ionic, spin and electronic degrees of freedom [2]. Katayama *et al.* reported a calculated displacement of soft phonon mode in perovskite-type SrTiO₃ of about 1 pm under the 80-kV/cm THz excitation [4]. Without an optical pump to excite the carriers, the intense THz pulse can only excite the lowest-lying phonon modes in halide perovskites, that enables us to explore the optical phonon lifetime and

phonon anharmonicity in the sub-picosecond to nanosecond timescale. Under this condition, the broadband infrared probe from TA may detect the coherent phonon information in halide perovskites. Using an intense THz pump and a THz probe (i.e. sub-bandgap excitation and probing), we can monitor the dynamics of impact ionization in the perovskites [4]. From TA results, we can unveil exciton and carrier dynamics. Hence, combining TRTS and TA results, we can investigate the dynamics of carriers, excitons, and phonon modes — the three degrees of freedom in lead halide perovskites and other novel materials.

8.2 Chiral materials and ultrafast techniques

A molecule or ion is called chiral when its mirror image cannot be brought to coincide with itself by any combination of rotations and translations. A chiral organic molecule and the molecule of its mirror image are called a pair of enantiomers. Different members of the pair of enantiomers can absorb left- and right-circularly polarized light differently.

It was discovered that chiral properties of organic molecules can be applied to inorganic semiconductors as well [5]. Chiral materials can exhibit circular dichroism (CD) [5,6], second-harmonic generation [7], ferroelectricity [8,9] and quantum properties [10]. Therefore, chiral materials are good candidates for chiro-optoelectronic applications including circularly polarized light photodetectors [11], circularly polarized LEDs [12], quantum communication [10] and spintronics [13,14].

Chiral halide perovskites are halide perovskites with the incorporation of chiral organic ligands. Chiral perovskites with the incorporation of a pair of enantiomers such as (R)-(+)- α -methylbenzylamine and (S)-(+)- α -methylbenzylamine (R-MBA and S-MBA) can show different absorbance of left- and right-handed circular polarized light [6]. Chiral perovskites are potential materials that combine the excellent electronic property of perovskites and chirality of chiral materials [15].

Transient absorption spectroscopy has been used to detect exciton dynamics in chiral polyfluorene-phenylene copolymer in tetrahydrofuran and in cholesteric

thin films [16]. Scholz *et al.* obtained an exciton lifetime of 410 ps, and the fast subpicosecond to picosecond migration of singlet excitons from the transient absorption spectra [16]. The TA technique has been used to systematically study exciton bleaching of chiral perovskites after photoexcitation [17]. The size of chiral perovskite nanocrystal decreases with decreasing chiral ligand concentration. Kim *et al.* found that the blue-shift of exciton bleaching was consistent with excitonic confinement due to the decrease in nanocrystal size [17].

Figure 8.2: Schematic of TR-OKE spectroscopy following Ref. [18]. Laser pulses are stretched to ~ 1 ps. The fs or ps laser pulse splits into a gating pulse and a pump pulse. The pump and probe beams are co-focused onto the sample by an achromatic lens. The transmitted probe beam is then collected by the combination of a quarter-wave plate ($\frac{\lambda}{4}$), a Wollaston prism (WP), and a balanced photodiodes (BPD).

TR-OKE is the time-domain variant of anisotropic Raman scattering [19]. Following the THz-TDS analysis described in Chapter 2, we can convert the time-domain data into frequency domain, and then obtain the spectra containing the Raman modes. Considering Ref. [18], based on optical-pump optical-probe technique, we can use TR-OKE spectroscopy to detect the phonon mode dynamics of the materials shown in Fig. 8.2. Combining TA, TRTS, and TR-OKE results on these materials, we can elucidate the dynamics of exciton, carrier, and the phonon mode dynamics in the chiral perovskites.

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